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SURVEY OF THE THERMOCHEMISTRY OF HIGH-ENERGY REACTIONS

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AF Avionics Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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Project No. 4040, Task No. 404003

(Prepared under Contract No. AF 33(616)-7835 by the IIT Research Institute, Chicago, (Ill., Elliott Raisen, Sidney Katz, and Karl D. Franson, authors)

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### FOREWORD

This report, Technical Report No. IITRI-C191-33, describes the thermodynamic and computational phases of a research program entitled "Study of New Materials Related to the Development of Radiant and Thermal Sources." The report covers the period from April 15, 1962, to August 14, 1963. The investigation was conducted at the IIT Research Institute and its predecessor organization, Armour Research Foundation, Technology Center, Chicago 16, Illinois, under the sponsorship of the Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. Jason W. Sarnow of the AF Avionics Laboratory served as Project Engineer. The work was performed under Contract AF 33(616)-7835 (IITRI Project C191).

Dr. Sidney Katz, Scientific Advisor, was the Project Leader. Dr. Elliott Raisen served as Group Leader of Thermochemistry and as Task Supervisor. Administrative direction was provided by Dr. J. I. Bregman, Assistant Director of Chemistry Research. Other participants in the work include Paul Ase, Robert H. Boes, Karl Franson, Richard Snow, Betty Isakson, Pat Llewellen, Roberta Patzer, Loretta Lucek, Gertrud Matuschkovitz, and Martha Williams.

### **ABSTRACT**

### SURVEY OF THE THERMOCHEMISTRY OF HIGH-ENERGY REACTIONS

This report describes the thermodynamic and computational phases of a survey of exothermic chemical reactions. The purpose of the survey was to ascertain the utility of these chemical reactions as radiation sources for a variety of applications.

All currently available thermochemical data were surveyed. Computer programs were prepared and enthalpies were obtained for all inorganic reactions for which data were adequate. Tabulations included reactions of metals with oxides, fluorides, chlorides, sulfides, phosphides, azides, nitrides, silicides, carbides, nitrates, nitrites, chlorates, perchlorates, chromates, and borides. Data for a total of about 20,000 reactions were obtained. The data for the individual reactions included a balanced chemical equation, and enthalpies and heats of reaction per unit weight and volume. Supplementary tabulations included listings in order of energies of the most energetic reactions in each class, graphical presentations of the reactions of all the metals with various oxidizing agents plotted against enthalpies. similar plots for the reactions of all the oxidants in different classes with various metals, and a total recapitulation of all the reactions in each category in grid form in descending order of energy per unit weight and per unit volume. An extension of this survey to include the detection of the free energies of the reactions is proposed.

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### I. INTRODUCTION

The use of pyrotechnic reactions for the production of radiant and thermal energy has generated an interest in highenergy reactions in this laboratory. As a result, we have been conducting theoretical and experimental studies of high-energy reactions for the past several years. The theoretical studies were concerned with systematic examination of the reactions of metals with different oxidizer systems in order to establish logical criteria for choosing reactions to be studied experimentally. The experimental phases were concerned with the chemical and radiative properties of the reactions and included manipulative studies to establish control over the burning properties of the reactions, calorimetric studies to compare experimental enthalpies with theoretical values, burning-rate studies as a function of the ambient atmosphere, differential thermal analysis and thermogravimetric studies to aid in the interpretation of the kinetics and mechanisms of the reactions, and studies of the spectroradiative properties in the visible and infrared regions of the spectrum.

The most important property of the reaction is its enthalpy, which determines the maximum amount of heat available after the reaction occurs. If the reaction is carried out adiabatically, this heat will raise the temperature of the products to a value which is determined by their specific heats. If the reaction is carried out isothermally, the thermal energy can be used for processes involving energy absorption. The reactions exhibiting high negative enthalpies were therefore of most interest.

Much of the present study was concerned with calculating reaction enthalpies and correlating them with the properties of the reactants and the prodects and with relationships in the periodic table. The periodic table and the rapidly increasing body of thermochemical data on heat capacities, entropies, and heats and free energies of formation provide a framework for examining and correlating the theoretical behavior of thermochemical reactions. For our practical purposes it was most useful to compare the energy content of the reactions on a volumetric basis, because most of our applications are volume-limited. Since weight limitations are important too, the gravimetric enthalpies were also determined.

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### II. SCOPE OF THE STUDY

### A. Reactions Surveyed

In earlier work 2600 reactions of metals with binary oxides and 50 reactions of metals with fluorides were examined by using manual computations. On the present program 60.000 high-energy reactions were examined by using a kemington-Rand Univac 1105 computer. Of these, about 20.000 reactions were printed by the computer and 10,000 of them were stored on magnetic tape for further operations. The remaining reactions were discarded either because they had positive enthalpies or because other reactions between the same reactants were found with greater negative enthalpy. In chlorate reactions, for example, eac set of reactants may undergo several different stoichiometric reactions to produce different combinations of oxides and chlorides of the constituent metals.

The scope of the theoretical survey is summarized in Table 1. Sixteen classes of oxidizer systems were examined. The data for oxides, fluorides, and chlorides were the most numerous, being represented by 145, 105, and 102 compounds each. The others ranged from 68 for the sulfides to 5 for the chromates. The possible reactions of all these oxidizers with as many as 68 metals were examined.

The data compiled for the oxides were also used in the calculations involving ternary oxidants such as the nitrates, nitrites, chlorates, and perchlorates, in which oxides occur as a product. All the oxide reactions were examined by use of the computer to produce a more complete set of such reactions than those calculated previously; over 20,000 reactions were examined in 6 hours. It is estimated that the same task would take about 1 hour by using an IBM 7090 computer and about 7 man-years by using manual methods.

In general, the perchlorates, chlorates, oxides, and nitrates are the most energetic classes of reactions, followed by the fluorides, nitrites, silicides, nitrides, sulfides, and carbides. The enthalpy of the most energetic reaction in each of these classes is listed in Table 2. The results of this survey were used as a guide in choosing reactions to be studied in the laboratory.

Table 1

SCOPE AND SUMMARY OF THEORETICAL SURVEY
OF THERMOCHEMICAL REACTIONS

Oxidizer Class	Number of Oxidizers	Number of Reactions Examined	Number of Reactions Printed	Enthalpy of the Most Energetic Reactions, cal/cc
Oxides	145*	20,994	9,636	-8279 to -4949
Fluorides	105	n.r.	105	-5586 to -3000
Chlorides	102	10,545	3,061	-3336 to -2593
Sulfides	68	n.r.	2,145	-3169 to -2553
Nitrides Azides	44 13	n.r.	1,575	-2478 to -1766 -3346 to -1795
Silicides	36	n.r.	302	-5153 to -480
Carbides	30	n.r.	386	-2532 to -1102
Nitrates Nitrites	18 8	n.r.	1,226	-7798 to -3468 -4670 to -3476
Phosphides	25	n.r.	500	-1254 to -18
Chlorates Perchlorates	7 9	16,384	800	-7853 to -6100 -9459 to -6099
Borides	8	n.r.	14	-2994 to -110
Chromates	5	2,920	114	-3845 to -1915
Organic fluorides	Examined	on a limite	ed basis man	ually

<sup>\*</sup>The data for 71 oxides were used in the nitrate and nitrite computations.

n.r. Not recorded.

Table 2

THE MOST ENERGETIC REACTION IN TERMS
OF VOLUMETRIC ENTHALPY IN EACH CLASS OF OXIDIZERS

Class	Reaction	Enthalpy, cal/cc
Perchlorates	$8Be + MgClO_4 = MgCl_2 + 8BeO$	-9459
Chlorates	$13Be + 4 Acclo_3 = 2Ag_2Cl + 12BeO + BeCl_2$	-8103
Oxides	$2Be + RuO_2 = Ru + 2BeO$	-8279
Nitrates	$5Be + 2LiNO_3 = LiO + 5BeO + N_2$	<b>-</b> 7798
Fluorides	$3Be + ReF_6 = Re + 3BeF_2$	-5586
Nitrites	$3Be + 2NaNO_2 = Na_2O + 3BeO + N_2$	-4670
Silicidos	3CoSi <sub>2</sub> + 19a = 3Co + 2BaSi <sub>3</sub>	-5153
Chromates	$4Be + 2PbCrO_4 = Pb_2O + 4BeO + Cr_2O_3$	-3845
Azides	9Be + BaN <sub>6</sub> * = Ba + 3BeN <sub>2</sub>	-3346
Nitrides	$2U + 3Fe_2N = 6Fe + U_2N_3$	-2478
Chlorides	$5Ce + ReCl_5 = 3Re + 5CeCl_3$	-3336
Sulfides	$8\text{Th} + 7\text{FeS}_2 = 7\text{Fe} + 2\text{Th}_4\text{S}_7$	-3169
Carbides	2Ta + Li <sub>2</sub> C <sub>2</sub> = 2Li + 2TaC	-2533

 $<sup>^*</sup>N_6$  represents  $(N_3)_2$ 

### B. Computer Input and Output

All the data used for the computer input were obtained from the sources shown in Table 3 in the order of preference indicated. The National Bureau of Standards Circular 500 was used as the primary source whenever possible. In all cases, the heat of formation at 298°K was used.

Table 3
SOURCES OF DATA FOR THERMOCHEMICAL REACTIONS

Property	Source, in Order of Preference
Heat of formation at 298°K (ΔH <sub>298</sub> )	Reference 1, 2, 4, 5
Molecular weight	Reference 5
Density	Reference 5
Melting point	Reference 1, 3, 5
Boiling point	Reference 1, 3, 5

Rossini, F. D., Wagman, D. D., Evans, W. H., and Levine, S. Selected Values of Thermodynamic Tables, National Bureau of Standards Circular 500, 1952.

<sup>&</sup>lt;sup>2</sup>Glassner, A. The Thermochemical Properties of Oxides. Fluorides and Chlorides to 2500°K, Argenne National Laboratories, No. 5750, 1957.

<sup>&</sup>lt;sup>3</sup>Hodgman, C. D., ed., Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, 1954-55.

<sup>&</sup>lt;sup>4</sup>Quill, L. L., ed., The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics, McGraw-Hill Book Co., 1950.

<sup>5</sup> Hodgman, C. D., ed., Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, 1960-61.

The input data consisted of the reactants and products, their heats of formation, and various of their physical properties: molecular weight, melting point, boiling point, and density. Computer programs were designed which combined all the reducing agents (metals) and oxidizers (oxides, chlorides, perchlorates, etc.) into balanced equations and calculated the enthalpy of the stoichiometric reaction. Reactions with positive enthalpies were discarded. Those with negative enthalpies were subjected to further computations to determine the gravimetric and volumetric enthalpies\* based on the reactants weight and volume. Then each reaction was printed together with the data for each component. This output was stored on magnetic tape for the further processing discussed later.

Much of the input data was printed, so that all the properties for each reaction were conveniently assembled in one place. Melting points and boiling points aid in determining practical uses for the reactions. Physical states of the reactants aid in date mining the feasibility of formulating and storing the materials. Melting points and boiling points of the products indicate potentially useful properties of the reactions. For example, if the products undergo a phase transition at the temperature of maximum radiative energy, the reaction products will tend to lib rate more of their energy at this temperature and thus increase the efficiency. Also, if gaseous products are desired for radiative or other purposes, reactions that have relatively low-boiling products can be selected. Conversely, if solid products are desired, reactions that have high-melting products can be selected. Assembling the input and calculated data in one place thus increases the versatility of the compilations.

The output consisted of the following input and derived data: a balanced equation, the reaction components, heats of formation at 298°K, the averaged densities of the components, the melting points of the components, the boiling points of the components, heat of the reaction on a molar basis, the reactions' averaged density, the heat of the reaction per unit weight of the reactants (the gravimetric enthalpy), the heat of the reaction per unit volume of reactants (the volumetric enthalpy), and the atomic numbers of the components. Output values were omitted when the data were too limited to allow the required calculation. For example, if the reactant density was unknown, the position for volumetric enthalpy was blank.

In this work the "volumetric enthalpy" is used to designate the heat of the reaction based on a stoichiometric mixture of reactants occupying a theoretical volume of 1 cc. Similarly, the gravimetric enthalpy is the corresponding heat of reaction based on a gram of reactants.

### C. Theory

A generalized equation for the reactions of a metal with a binary compound is:

$$z A + y B_x^C_w \longrightarrow x y B + A_z^C_{yw}$$
 (1)

where A and B are electropositive elements (metals); C is an electronegative element (O, F, Cl. S, C, B, N, H, etc.); and z, y, x, and w are the constants for the stoichiometric reaction after the coefficient of the last term is adjusted to unity. The metal A reduces the compound B C to form the metal B and the compound of metal A. In order to calculate the energy per unit volume of reactants, the following equation is derived:

$$\Delta H_{CC} = -\frac{\Delta H_{A_{z}C_{yw}} - y \Delta H_{B_{x}C_{w}}}{z V_{A} + y V_{B_{x}C_{w}}} = \frac{\Delta H_{AO_{x}} - y \Delta H_{BO_{x}}}{z V_{A} + y V_{BO_{x}}}$$
(2)

where  $\Delta H_{CC}$  is the heat of reaction per unit volume of reactants; V is the gram-atomic and gram-molecular volume of the respective reactants, i.e., the atomic or molecular weight divided by the density; and

$$^{\Delta H}_{
m AO_{_{_{f X}}}}$$
 and  $^{\Delta H}_{
m BO_{_{_{f X}}}}$ 

are the molar heats of formation of the products and the reactants, respectively.

To obtain a large energy per unit volume of reactants, it is evident that the heat of formation of the products

$$^{\Delta H}{}_{A_{\mathbf{Z}}C_{yw}}$$

should be large, the heat of formation of reactants

$$^{\Delta H}_{\mathcal{B}_{\mathbf{x}}^{\mathcal{C}_{\mathbf{w}}}}$$

and the gram-atomic and the gram-molecular volumes of the reactants

should be small, and the coefficients y and z should also be small. According to the usual convention, a negative  $\Delta H$  is considered as energy output. Thus, in this analysis a "large"

$$^{\Delta H}\mathbf{A_{z}^{C}yw}$$

in reality signifies a large negative number and a "small"

$$^{\Delta H}_{\mathbf{B_{x}^{C}_{w}}}$$

signifies a small negative number or even a positive number; hence a large negative value for  $\Delta H/cc$  is desired.

The use of Equation 2 can be demonstrated by examples from the oxide systems. In general, the oxide of the reducing agent should have a heat of formation

$$^{\Delta H}$$
AzCyw

exceeding -250 kcal and the reducing agent itself a gram-atomic volume less than 15 cc, while the oxidizing agent should have a heat of formation

$$^{\Delta H}\mathbf{B}_{\mathbf{x}}\mathbf{C}_{\mathbf{w}}$$

less than 100 kcal and a gram-molecular volume less than 35 cc. If the components of a reaction satisfy these four conditions, the reaction will be highly energetic, except then the combination of valences produces large values of y and z which nullify the other factors. The y term is especially significant because of its influence on the numerator. The value of y is not a constant for an oxide but is rather a function of the valence of element A in the reaction, and it can only be found by balancing the reaction and adjusting the coefficient of the  $A_{\rm Z}C_{\rm VW}$  term to unity. Various exceptions occur when one of the four factors is outside the specified range, but the extreme value of one or more of the other factors compensates.

The reducing agents Be, Mg, La, and Nd and the oxidizing agents WO3, Fe<sub>2</sub>O<sub>3</sub>, OsO<sub>4</sub>, and Tl<sub>2</sub>O<sub>3</sub> are examples of the various possibilities. For example, the low gram-atomic volumes of Be and Mg (4.96 and 14.0 cc, respectively) compensate for the rather low heats of formation of their oxides (-146.0 and -148.9 kcal, respectively), while the large heats of formation of the oxides of La and Nd (-433 and -436 kcal, respectively) compensate for the high gramestomic volumes of the metals (50 and 46 cc, respectively). Similarly, the low grammolecular volumes of WO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> compensate for their rather high heats of formation. On the other hand, the low heats of formation of OsO<sub>4</sub> and TlO<sub>3</sub> (-93.6 and -84 kcal, respectively) compensate for their relatively large gram-molecular volumes (51.8 and 44.8 cc, respectively).

### D. Presentation of Data

Initially the computer was programmed to take each metaloxidizer compound in alphabetical order and to treat it as the
product of the reaction. When the oxidized metal exists in
several valence states, each state was treated as a separate
compound. All the other compounds were taken successively in
alphabetical order and treated as reactants. A balanced
equation was computed by using the appropriate metal from each of
the compounds in the reaction. The enthalpy of the reaction was
then computed by taking into account the coefficients in the
balanced equation. If the enthalpy was negative, the gravimetric
and volumetric\* enthalpies were calculated and all the data for
each reaction were printed. If the enthalpy was positive, the
reaction was ignored\*\* and the program went on alphabetically to
the next compound. This was done for each metal. Later the order
of choosing reactions was based on the reactant oxidizer.

Thus all the reactions of one metal with a series of reactants which yield the same product were printed. When the product exists in a higher valence form, the same process was repeated for the higher valence form. Then the next product was treated in alphabetical order. This type of output, represented by 1 in Table 4, was printed and also stored on magnetic tape. In order to make the data more readily available, the magnetic tape was processed many times with different programs to produce the other types of outputs shown in Table 4. These outputs all contain essentially the same data but arranged in different formats. All the outputs were obtained on volumetric and gravimetric bases.

It would be impractical to reproduce the prodigious amount of material available from the computer. The results are summarized and discussed in this report, and representative data sheets for each type of oxidizer system are included for illustrative purposes.

The volumetric enthalpies were calculated from the density of condensed phases only.

Reactions with positive enthalpies are not of interest here. If they were included, twice as many reactions would result.

Table 4

# TYPES OF COMPUTER OUTPUTS

Summarize all the data for each reaction in one place.	Rapid determination of the most energetic reactions of each oxidizer class on a gravimetric basis. This indicates the maximum energy for a unit weight of reactants.	Rapid determination of the most energetic reactions of each oxidizer class on a volumetric basis. This indicates the maximum energy for a unit volume of reactants.	
Compilation of balanced equations together with input and output data for each constituent.	A list of all the reactions for each system in order of decreasing negative values of gravimetric enthalpy.	A list of all the reactions for each system in order of decreasing negative values of volumetric enthalpy.	
Type 1	7	m	
Oxidizer Classes Programmed Oxides Chlorides Sulfides Nitrides Azides Silicides Carbides Nitrites Nitrites Phosphides Chlorates	Chromates Oxides Chlorides Chlorates Perchlorates	Chromates  Oxides Fluorides Chlorides Sulfides Nitrides Azides Silicides Carbides Nitrates Nitrates Chlorates Borides	Chromates

Purpose	Helpful in finding the best oxidizer with a particular metal or for examining the periodic behavior of a metal with the different oxidizers, based on a unit weight of reactants.	Helpful in finding the best oxidizer with a particular metal or for examining the periodic behavior of a metal with each oxidizer, based on a unit volume of reactants.	Helpful in finding the best metal for a particular oxidizer, or for examining the periodic behavior of an oxidizer with the different metals, based on a unit weight of reactants.	Helpful in finding the best metal for a particular oxidizer, or for examining the periodic behavior of an oxidizer with the different metals, based on a unit volume of reactants.	The most concise summary of the enthalpies of all the reactions of each class. This table indicates the most energetic metals and oxidizers at a glance, based on a unit weight of reactants.	The most concise surmary of the enthalpies of all the reactions of each class. This table indicates the most energetic metals and oxidizers at a glance, based on a unit volume of reactants.
Description	A list of all the data used for the graphs. Graphs of the gravimetric enthalpy of one metal versus the oxidizers for each metal.	A list of all the data used for the graphs. Graphs of the volumetric enthalpy of one metal versus the oxidizers for each metal.	A list of all the data used for the graphs. Graphs of the gravimetric enthalpy of one oxidizer versus the metals for each oxidizer.	A list of all the data used for the graphs. Graphs of the volumetric enthalpy of one oxidizer versus the metals for each oxidizer.	A chart of the gravimetric enthalpies of all the reactions for each system listed in general descending order from left to right, and from top to bottom.	A chart of the volumetric enthalpies of all the reactions for each system listed in general descending order from left to right, and from top to bottom.
Type	4	u	φ	7	ω	σ
Oxidizer Classes	Oxides Chlorides Chlorates Perchlorates Chromates	Oxides Nitrates Chlorides Chlorates Parchlorates Chromates	Oxides Chlorides Chlorates Perchlorates Chromates	Oxides Chlorides Chlorates Perchlorates Chromates	Oxides Chlorides Chlorates Perchlorates Chromates	Oxides Chlorides Chlorates Perchlorates Chromates

### III. DISCUSSION OF THERMOCHEMICAL DATA

### A. Fluoride Reactions

The molecular, gravimetric, and volumetric enthalpies of about 5000 reactions resulting from the combination of 50 metals with 105 fluorides were calculated and compiled on the computer. The reactions of beryllium with cobalt trifluoride, ferric fluoride, and stannic fluoride are particularly energetic; beryllium fluoride is formed in these reactions.

Table 5 is a list of fluoride reactions with negative enthalpies in excess of -3000 cal. The reactions are all of the form:

$$A + BF = B + AF$$

where BF and AF are the reactant and product fluorides, respectively, and A and B are the corresponding metals. Each reaction is identified by the reactant and product fluoride and their molecular coefficient: the metal reactants and products are omitted from the tabulation.

As a group, the fluorides are a highly energetic series of reactions. Experimental study of many of these reactions should prove interesting, especially those with very high enthalpies and those with products that have low melting or low boiling points. The reactions with the following products merit further study: mercury, cobalt, tin, iron, silver, bismuth, antimony, manganese, nickel, gallium, cadmium, chromium, beryllium fluoride, germanium fluoride, neodymium fluoride, praseodymium fluoride, and lithium fluoride.

Figure 1 illustrates the periodic behavior of the enthalpies of the fluoride reactions. The metals are plotted by atomic number along the abscissa, and the volumetric enthalpies of their reactions with cobalt trifluoride are shown on the ordinate. Cobalt fluoride was chosen as the reactant because most of its reactions are highly energetic. A representative reaction is:

$$3Be + 2CoF_3 = 2Co + 3BeF_2;$$
  $\Delta H = -380.2 \text{ kcal}$ 

Here,  $\Delta H$  is the molar enthalpy. The enthalpy in Table 5 is the heat of the reaction on a volumetric basis in terms of calories per cubic centimeter of reacting material, in this case -5111 cal/cc.

All the available data are plotted in Figure 1, and the various points are connected by solid, dotted, or dashed lines to indicate their relationships within the periodic table. The solid lines connect metals with adjacent atomic numbers, the dotted lines connect members of the same group, and the dashed

lines connect the members of a B group (transition metals). The three subfigures IA, B, and C emphasize each of these relationships.

Figure 1A, in which the adjacent atomic numbers are connected, illustrates the overall periodic behavior of the enthalpies. In general, the Group II elements (beryllium, magnesium, calcium, strontium, and barium) establish the peaks in the energy outputs (i.e., the largest negative enthalpies) and the Group I elements (lithium, sodium, potassium, rubidium, and cesium) establish the minima. The curve is irregular in the neighborhood of strontium and barium because the Group IIIB metals (yttrium, lanthanum, and the rare earths) and the Group IVB metals (titanium, zirconium, and hafnium) have unusually small atomic volumes and their fluorides have relatively high heats of formation.

The elements establishing the peaks in the energy curve are characterized by one or more of the following:

The electronic configuration of their valence orbitals. Their outermost orbital has two electrons, and the next-to-outermost orbital has either one or two electrons.

Their electronic configuration in the fluorides. They all have the rare gas configuration, s<sup>2</sup> or s<sup>2</sup>p<sup>5</sup>.

The high heat of formation of the fluoride relative to the fluoride of their nearest neighbors.

Their low gram-atomic volumes.

Groups IIIB and IVB tend to react more energetically than Group II. The fluoride curve is similar to the analogous oxide and nitrate curves, with a few exceptions. Aluminum, for instance, is less energetic than magnesium in the fluoride system and more energetic in the oxygen system, because of the unusually high heat of formation of the oxide.

The relationship of the elements within Groups IA, IIA, IIIA, and IVA is shown in Figure 1B. Except for boron in Group IIIA, the energies of the reactions of cobalt trifluoride within the elements of a group diminish with increasing atomic number. A group relationship is also apparent. In decreasing order of energy, they follow the sequence Group IIA, IIIA, IVA, and IA.

Figure 1C shows the relationship of the elements within the transition metal groups. Groups IIB (zinc and cadmium), VB (vanadium, niobium, and tantalum), and VIB (chromium, molybdenum and tungsten) are similar to Groups IA, IIA, IIIA, and IVA in that the energy tends to decrease with increasing

Table 5

FLUORIDE REACTIONS\* WITH HIGHEST NEGATIVE ENTHALPIES

			Me	tal	Fluo	oride
Enthalpy, cal/cc	Reactant	Product	m p.,	оС р р.,	m.p.,	p.p.,
-5586	ReF <sub>6</sub>	3 BeF <sub>2</sub>	3147		800	
-5206	CF <sub>4</sub>	2 BeF <sub>2</sub>	4400			
-5112	2 CoF <sub>3</sub>	3 BeF <sub>2</sub>	1493	3100		
-5015	ReF <sub>6</sub>	3 YF <sub>3</sub>				
-4960	HgF <sub>2</sub>	BeF <sub>2</sub>	-39	357		
-4926	ReF <sub>6</sub>	2 CeF <sub>3</sub>			1460	
-4870	ReF <sub>6</sub>	2 LaF <sub>3</sub>				
-4830	SnF <sub>4</sub>	2 BeF <sub>2</sub>	232	2337		
-4820	ReF <sub>6</sub>	$2 \text{ NdF}_3$			1410	
-4809	ReF <sub>6</sub>	2 PrF <sub>3</sub>			1370	
-4765	NbF <sub>5</sub>	5 BeF <sub>2</sub>				
-4683	3 CF <sub>4</sub>	4 YF <sub>3</sub>				
-4648	FeF <sub>2</sub>	BeF <sub>2</sub>	1535	2800		
-4603	AgF <sub>2</sub>	Ber <sub>2</sub>	961	2193		
++563	CoF <sub>3</sub>	YF <sub>3</sub>				
-4534	$3 \text{ HgF}_2^-$	2 YF <sub>3</sub>				
-4527	3 CF <sub>4</sub>	4 LaF <sub>3</sub>				
-4460	CoF <sub>3</sub>	LaF <sub>3</sub>				
-4450	3 HgF <sub>2</sub>	2 LaF <sub>3</sub>				
-4342	$3 SnF_4$	4 YF <sub>3</sub>				
-4272	3 NbF <sub>3</sub>	5 YF <sub>3</sub>	2478	3700		
-4268	3 AgF <sub>2</sub>	2 YF <sub>3</sub>		•		
-4267	$3 \operatorname{SnF}_{4}^{-}$	4 LaF <sub>3</sub>				
-4216	3 AgF <sub>2</sub>	2 LaF <sub>2</sub>				
-4213	3 FeF <sub>2</sub>	2 YF <sub>3</sub>				
-4202	3 NbF <sub>5</sub>					
-4156	3 FeF <sub>2</sub>					
-3889	B <sub>1</sub> F <sub>3</sub>	YF <sub>3</sub>	271	1420		
-3869	BiF <sub>3</sub>	LaF <sub>3</sub>				
-3821	•	5 BeF <sub>2</sub>	630	1440		
-3707	2 TaF	5 Ber <sub>2</sub>				

Table 5 (cont.)

<del></del>	<del></del>	·····	Me	tal	Fl	uoride
Enthalpy, cal/cc	Reactant	Product	m.p.,	b.p.,	m.p.,	p.p.,
-3704	2 VF <sub>5</sub>	5 BeF <sub>2</sub>	1730	3000		
-3611	AgF <sub>2</sub>	2 LiF			845	1681
-3601	3 SbF <sub>5</sub>	5 LaF <sub>3</sub>				
-3601	MoF <sub>6</sub>	3 BeF <sub>2</sub>	2610	4800		
-3589	3 SbF <sub>5</sub>	5 BeF <sub>2</sub>				
-3573	2 MnF <sub>3</sub>	3 BeF <sub>2</sub>	1244	2087		
-3568	NiF <sub>2</sub>	BeF <sub>2</sub>	1455	2800		
-3564	3 TaF <sub>5</sub>	5 LaF <sub>3</sub>				
-3544	3 TaF <sub>5</sub>	5 BeF <sub>2</sub>				
-3502	3 VF <sub>5</sub>	5 LaF <sub>3</sub>				
-3478	3 VF <sub>5</sub>	5 YF <sub>3</sub>				
-3427	MoF <sub>6</sub>	2 LaF3				
-3424	2 GaF <sub>3</sub>	3 BeF <sub>3</sub>	30	937		
-3394	MoF <sub>6</sub>	2 BeF <sub>2</sub>				
-3392	VF <sub>4</sub>	2 BeF <sub>2</sub>				
-3376	MnF <sub>3</sub>	$LaF_3$				
-3323	3 NiF <sub>2</sub>	2 YF <sub>3</sub>				
-3329	MnF <sub>3</sub>	YF <sub>3</sub>				
-3322	2 SbF <sub>3</sub>	3 BeF <sub>2</sub>				
-3320	2 FeF <sub>3</sub>	3 BeF <sub>2</sub>				
-3259	$^{\mathrm{GaF}}_{3}$	$LaF_3$				
-3214	sbr <sub>3</sub>	LaF <sub>3</sub>				
-3202	FeF <sub>3</sub>	LaF3			•	
-3192	GaF <sub>3</sub>	YF <sub>3</sub>				
-3183	3 VF <sub>4</sub>	4 BeF <sub>2</sub>				
-3157	SbF <sub>3</sub>	YF <sub>3</sub>				
-3144	3 AgF	LaF <sub>3</sub>				
-3143	CdF <sub>2</sub>	BeF <sub>2</sub>	321	767		
-3109	3 CrF <sub>3</sub>	3 BeF <sub>2</sub>	1900	2480		
-3098	3 AgF	YF <sub>3</sub>				
-3070	3 CdF <sub>2</sub>	2 LaF <sub>3</sub>				
-3038	3 CrF <sub>3</sub>	LaF <sub>3</sub>				

<sup>\*</sup>The first reaction, for example, is: 3 Be + ReF<sub>6</sub> = Re + 3 BeF<sub>2</sub>.

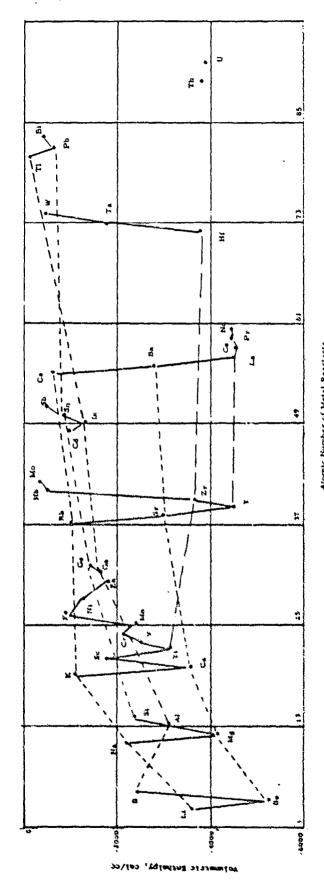


Figure 1 Volumetric Enthalpies of Reactions of Metals With Cof,

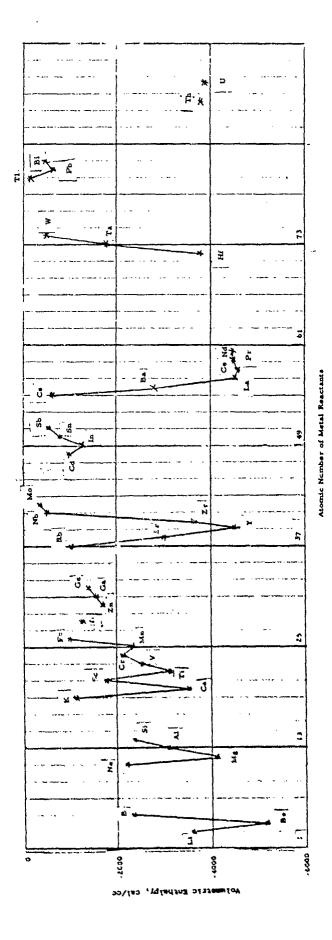


Figure 1A volumetric enthalfuls of retals, with  $\mathsf{cof}_{\mathfrak{z}}$ 

17

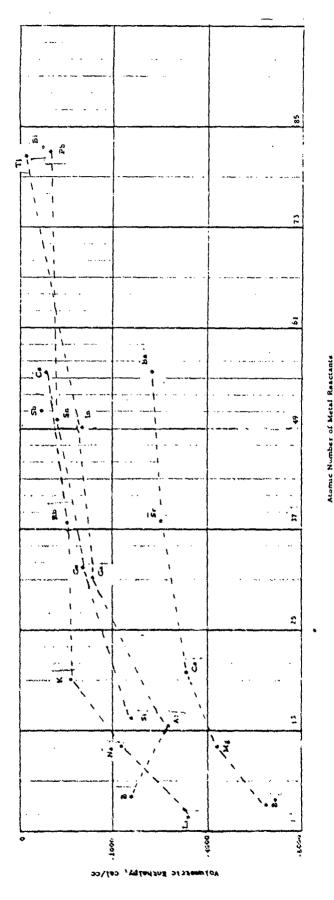
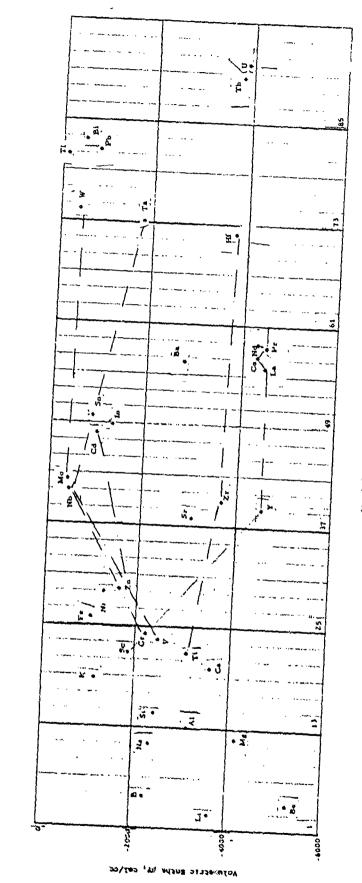


Figure 1 is Volumetric enthalpies of reactions of metals with  $\operatorname{Cof}_{\mathfrak{z}}$ 

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Alomic Number of Metal Reactable

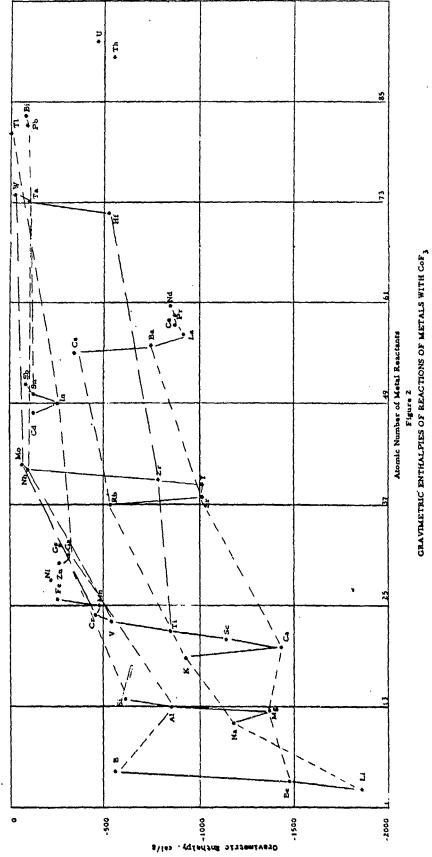
| Figure | | C|
| FOLUMETRIC| ENTHALPIES OF REACTIONS OF METALS WITH COF 3

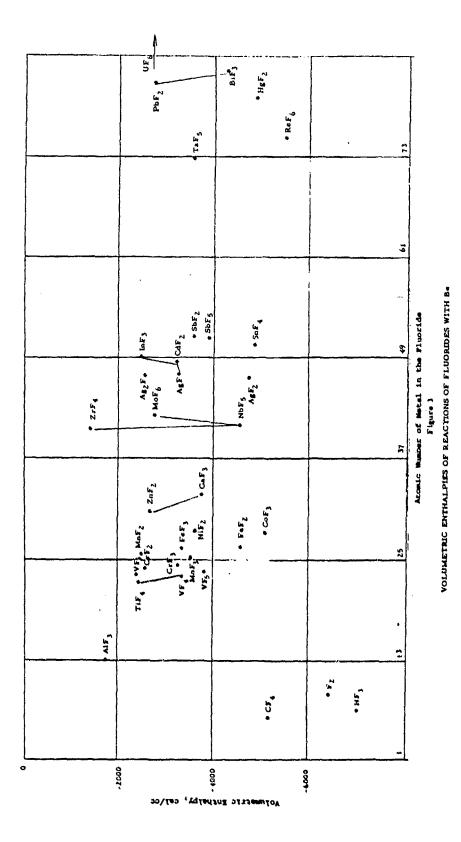
atomic number. Groups IIIB (scandium, yttrium, and lanthanum, and the rare earth elements) and IVB (titanium, zirconium, and hafnium) exhibit the opposite behavior and increase in energy with increasing atomic number. This behavior is due primarily to the small increase, or even decrease in the atomic volume of the elements in these groups with increasing atomic number, caused by the lanthanide contraction. Groups IIIB and IVB are the most energetic, and Groups IIB, VB, and VIB are the least energetic.

Similar relationships for the gravimetric enthalpies (heat output per gram of reactants) are illustrated in Figure 2. A few differences are observed because densities of the reactants vary. Since the volume is not considered, the effect of the lanthanide contraction is not evident, and Groups IIIB and IVB exhibit a normal behavior, with their energy decreasing with increasing atomic number. On the gravimetric basis, lithium is more energetic than beryllium, scandium more energetic than titanium, and Group I more energetic than Group III. The gravimetric enthalpies are lower than the volumetric ones because the densities of the reactants are more than unity in all cases.

Although the volumetric enthalpies were considered more significant for the present studies, because the establishment of a maximum energy in a fixed volume is usually desired, the gravimetric enthalpies were also considered in choosing the reactions to be studied experimentally. Less information is available on volumetric enthalpies because the densities of the reactants are often not known.

Figures 1 and 2 emphasized the effect of the metal on the enthalpy of the reactions. Figures 3 and 4 emphasize the effect of the fluoride. The volumetric and gravimetric enthalpies of the reactions of the fluorides with beryllium are plotted in Figures 3 and 4 on the ordinate, with the atomic number of the metal in the fluoride shown on the abscissa. A periodic behavior is apparent but is difficult to specify because, fluorides of each metal can exist in different valence states within a group the energy decreases with increasing atomic number; since the metals are in the oxidized form, the order of the groups is reversed. Thus Groups IIIB and IVB are the least energetic when the metal fluoride, rather than the metal, is used as the reactant. Groups V, VI, VII, and VIIIB, represented by vanadium, chromium, manganese, iron, cobalt, molybdenum, tungsten, rhenium, and osmium fluorides, are the most energetic When a metal forms more than one fluoride, the one with the greatest number of fluorine atoms is usually the most energetic. The iron flurides are exceptions, FeF<sub>2</sub> being more energetic than FeF<sub>3</sub>. The trends illustrated in the figures are similar for the other fluorides and metals, except for displacement of the vertical scale





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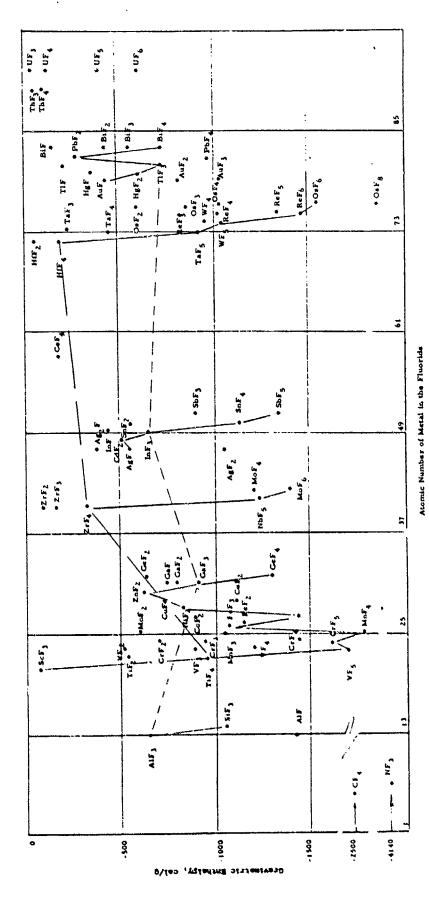


Figure 4
GRAVIMETRIC ENTHALPIES OF REACTIONS OF FLUORIDES WITH Be

### B. Oxide Reactions

A total of 20,994 reactions involving 145 oxides was examined, and the data for 9636 reactions were printed. Of the 9636 reactions, about half were pertinent to the present study; reactions with positive and negative enthalpies were inadvertently included in the output. The oxides form a highly energetic class of reactions, with volumetric enthalpies up to 8279 cal/cc. The oxide systems, including the perchlorates, chlorates, and nitrates, are the most energetic of all the classes of reactions examined. The oxide parameters tend to dominate and, as a result, the trends in perchlorate, chlorate, and nitrate reactions are similar to those in the oxide reactions.

Representative computer outputs, including some of the more energetic reactions, are shown in Table 6. In this format all the data for each reaction are assembled in one place. Several reactions with positive enthalpies are shown. On a molar or gravimetric basis, they are the same as the reverse reaction with a negative enthalpy. On a volumetric basis, the results for the reverse reaction are slightly different, since the reactants and products have different densities. This is illustrated by the reaction of silver with cobalt monoxide and the reverse reaction of cobalt with silver oxide. It is also demonstrated by the fact that the reaction between cobalt and silver oxide is more energetic when the cobalt monoxide, rather than the dicobalt trioxide, is produced. This is not obvious from Table 6 because only the reaction with the greatest thermal output is printed when more than one reaction is possible between any two reactants,

The most energetic oxide reactions are shown in Tables 7 and 8 on volumetric and gravimetric bases, respectively. On the volumetric basis, the best reducing metals are the lower members of Groups IIA and IIIA (beryllium, magnesium, aluminum, and boron), the Group IVB elements (titanium, zirconium, and hafnium), and the IVF and VF elements (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, gadolinium, etc., and thorium and uranium). On the gravimetric basis, the same elements are the best reducing metals, with a few notable exceptions. Lithium is one of the best metals on a gravimetric basis but is very poor on a volumetric basis because of its extremely low density. On the other hand, the extremely high densities of thorium and uranium cause them to be much more effective on a volumetric than on a gravimetric basis.

The most effective oxidizers on a volumetric basis are the oxides of ruthenium, nitrogen, rhenium, sulfur, silver, osmium, selenium, manganese, carbon, cobalt, arsenic, lead, and copper. The most effective oxidizers on a gravimetric basis are the oxides of nitrogen, carbon, sodium, sulfur, ruthenium, molybdenum, indium, potassium, and chromium.

Table 6

DATA ON REACTIONS OF VARIOUS METALS WITH OXIDES

		-	0 7 6	11	2 AC	+	CGO
	8	+	Ag 2		- 1		
Host of formation			-7.31		20 20 1		1.28.41
cula			- 6		10,50		8.15
Density			#T° /		960.80		00.006
point,	320.90		200.000		2193.00		00.006
point, oc	707°00 53 55						
Heat of reaction, Kcal	י ה						
<b>נ</b> יי	-155.60						
Gravimetric enthalpy, cal/9	178						
- 1	2 Ce	+	3 Ag 20	u	8 Ag	+	Ce <sub>2</sub> 0 <sub>3</sub>
			il .				-435.00
Heat of formation	6.		231 76		107.87		328.26
Molecular weight	140.13		• (		10.50		06.9
Density	77 5 00		•		960.80		1692.00
point,	29.00						
point, c	-413.08						
Heat of reaction, Mcd.	7.01						
ov. cal	4.						
,	- 2968 - 24						
	පි	+	$Ag_2^0$	ll	2 Ag	+	CoO
			-7.31				-57,20
Heat of formation	58.94		231.76		107.87		
Molecular weight	ີ່ ໝໍ		7.14		10.50		•
	1493.00		300°00		960.80		1800.00
	å				2193.00		
Heat of reaction, kcal	٥						
ts' density	7.44						
Gravimetric enthalpy, cal/g	1.						
6 7 3							

Table 6 (cont.)

							7
	2 Ag	+	CoO	11	ဝ	+	Ag 2
			1				-7.31
Heat of formation	107.87				58,94		231.76
Molecular Weight	10.50		ູ້ ຄ		08.30		300.00
Density Melting point, °C	960.80		Tennan		3100.00		
	49.89						
	8.63						
Reactants consists Gravimetric enthalpy, cal/g	171,64						
cal/	1480°11				1		
	2 A1	+	3 COO	11	3 Co	+	A1 2 <sup>0</sup> 3
			10				
Heat of formation	0		•		58.94		
ula	26.98		5.70		8.50		
Density	660,099		•		1493.00		2015.00
	2327.00				3100.00		
Heat of reaction, kcal	-227.49						
rs' density	-816.02						
, O	-3828.99						,
	2 As	+	3 000	11	3 Co	+	As 203
			4				56.
Heat of formation			74.94		L)		197.82
- (U	74.92		5,70		۰		4.13
Density	61°C		1800.00		1493.00		313.00
point	817.00		ļ Ī		100,		င်
Boiling point, 'C keal	15,45						
reaction, m	5.71						
Reactants centraly, cal/g	41.24						
, cal/	735.50						

Table 6 (cont.)

	6 Ag	+	Co203	11	2 Co	+	3 Ag 20
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	107.87 10.50 960.80 2193.00 118.08 8.68 145.22	,	-140.00 165.88 5.18 895.00		58.94 8.90 1493.00 3100.00		-7.31 231.76 7.14 300.00
	2 A1	+	$c_{0203}$	11	2 Co	+	A1 203
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	26.98 2.70 660.00 2327.00 -259.09 4.23 -1178.54 -4983.12		-140.00 165.88 5.18 895.00		58.94 8.90 1493.00 3100.00		-399.09 101.94 3.97 2015.00 3500.00
	2 As	+	Co203	П	2 Co	+	As 203
Heat of formation Molecular weight Density Melting point, °C Bolling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	74.92 5.73 817.00 817.00 -16.15 5.43 -51.15		-140.00 165.88 5.18 895.00		58.94 8.90 1493.00 3100.00		-156.15 197.82 4.15 313.00 460.00

Table 6 (cont.)

	6 Li	+	0,00	11	2 Co	+	3 Li 20
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	0 400 000		-140.00 165.88 5.18 895.00		58.94 8.90 1493.00 3100.00		-142.40 29.88 2.01 1700.00
	3 Mg	+	Co203		2 Co	+	3 MgO
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	24.32 1.74 650.00 1120.00 -291.52 3.23 -1220.57		-140,00 165.88 5.18 895.00		58.94 8.90 1493.00 3100.00	,	-143.84 40.32 3.58 2800.00
	3 Mn	+	CO203	11	2 Co	+	3 MnO
Heat of formation .  Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	54.94 7.20 1244.00 2087.00 -136.00 6.02 -411.25		-140.00 165.88 5.18 895.00		58.94 8.90 1493.00 3100.00		-92.00 70.93 5.43 1650.00

Table 6 (cont.)

	4 Ag	+	Mno	11	Mn	+ 2 A	Ag 20
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	107.87 10.50 960.80 2193.00 109.89 8.88 211.97 1881.95		-124.50 86.93 5.03 535.00		54.94 7.20 1.244.00 2087.00	231 231 300	7.31 1.76 7.14 0.00
	4 A1	+	3 MnO <sub>2</sub>	u	3 Mn	+ 2 A	1203
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Reat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	26.98 2.70 660.00 2327.00 -424.68 4.02 -1151.80		-124.50 86.93 5.03 535.00	•	54.94 7.20 1244.00 2087.00	2015 2015 3500	9.09 1.94 3.97 0.00
	4 As	+	3 MnO <sub>2</sub>	d	3 Mn	+ 2 A	.s <sub>2</sub> 0 <sub>3</sub>
Eat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	74.92 5.73 817.00 817.00 61.20 5.38 109.19 587.24		-124.50 86.93 5.03 535.00		54.94 7.20 1244.00 2087.00	-15 19 31 46	6.15 7.82 4.15 3.00 6.00

Table 6 (cont.)

	2 Be	+	Mno <sub>2</sub>	11	Mn	+	2 BeO
1							-146.00
Hear or Formation Molecular Weight	•		o u		54.94 00.7		ຸ່ຕ
Density			•				Ö
point,	'n c		) )				ġ.
Heat of reaction, what	ຕໍ						
	_1595.91 _6194,56						
			- 1		1	+	7
	4 Bi	+	3 MnO <sub>2</sub>	ii	3 ran	+	2 B1 2 3
			4.5				-137.90
Heat of formation	208,99		86		٠		466.00
Molecular Welght	g		0.				2000
4	7		0		1244.00		1890.00
Reliting point, of	0						•
Heat of reaction, kcal	97.70						
s' density	80.08						
Gravimetric enthalpy, cal/g	712.15						
6.7.7	U	+	Mn0,	11	Mn	+	CO
			1				0 70
Heat of formation .	•		-124.50				44.01
ula			ے ٹر		7, 20		7,9
Density	i u		9				2
	4347.00		•		_		8.5
Boiling point, "C	30						
Ú	4						
Reactants Tensity Cal/g	307.						
٠,	1345.30						

Table 6 (cont.)

	1		2 N	+ 4 Ag,0
	8 Ag			1 (
Heat of formation		2.31 92.00	14.01	-7.31 231.76 7.14
Molecular worg Density	10.		<del>1</del> )	Ċ.
point, °C point, °C				
reaction, Kcal s. density	196			
Volumetric enthalpy, cal/cc	6			
	8 A1	$+ 3 N_2 O_4 =$	N 9	+ 4 Al <sub>2</sub> 0 <sub>3</sub>
		7	ני	-399.09
Heat of lotmarton Molecular weight	26.98	92.00 1.49	14.01	m
Density of	660.00			• ,
point, °C	23.27.00			) )
Heat of reaction, kcal	1.86			
Reactants' density Gal/9 Gravimetric enthalpy, Cal/9	-3259.77 -6050.32			
	8 As	+ 3 N <sub>2</sub> O <sub>4</sub>	N 9 ==	$+ 4 \text{ As}_2^{0_3}$
		. اد		•
deat of formation	6		14.01	97.
Molecular weight		1.49	.81	313,00
Density	0,7	3		
point, °C	о, <sub>п</sub>			
Heat of reaction, kcal	, e			
Reactants' density Gravimetric enthalply, cal/9				
(+5)				

Table 6 (cont.)

	4 Be	+	N <sub>2</sub> O <sub>4</sub> "	H	2 N	.1	4 Be0
			പ്ത				
Heat of formation Molecular Weight		•	92.00 1.49		14.01 .81		3.01
Density	1. 283.		9				3
point, c	2970.00						·
rt e	מ מרק						
Gravimetric enthalpy, cal/g	-45/3.60						
1	8 B1	+	$^{N}_{2}^{O}_{4}$	ii	N 9	+	4 Bi 203
			2.31				
Heat of formation	208.99		92.00		14.01		ρα
Molecular Weight			Ä,		18.		
Density	271.		97.00				
point, °C	4 20 7 0 1						
Heat of reaction, kcal							
[60]	-286.73						
Gravimetric enthalpy, cal/cc	570						
-	2 C	+	N 204	li	2 N	+	2 co <sub>2</sub>
							4.0
Heat of formation	12.01		92.00		14.01		င္စ
Molecular Weight	2.25		1.49		Ţρ.		-56.20
point,	25.00		• -i				78.5
Boiling point, oc	-190.41						
s' density	,						
Gravimetric enthalpy, cal/g	_1641.15			Ì			

Table 6 (cont.)

	24 7	+ Pb0.	11	Pb	+ 2	Ag C
1		66.				-7,31
Heat of FollideLon	~	239.21		2,5		•
MOLECULAL MCLUMA	10	δ		11.3		٠ ١
Melting point, °C	0	•		327,40		,
	93			2		
Heat of reaction, kcal	PP (					
ts' density	<b>)</b> (					
Gravimetric enthalpy, cal/g	773,27					
. 1						'
•	4 Al	+ 3 PbO <sub>2</sub>	11	3 Pb	+	2 AL 203
						0.66
Heat of formation		20°7			•	101.9
		42.862 85.0		11,34		(C)
Density	, i	0000				15.
point,		290.062				0
point, °C	, , ,			) )		
Heat of reaction, kcal	, ני					
ts' density	, 6					
	-5149.20					
1						
	4 As	+ 3 PbO <sub>2</sub>	11	3 Pb	+	2 As 203
		ı				56.1
most of formation		4				1001
	9	239.21		201.21		, 4
	٥	u				יי ייי
Densicy	<u>ر</u>	3		327.		, c
politing points	3					200
Heat of reaction, Xcal	ကို၊					
s' density	، م		٠			
Gravimetric enthalpy, cal/g	-117.00					
(73						

Table 6 (cont.)

	2 Be	+	PbO	11	Pb	+	2 BeO
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	9.01 1.85 1283.00 2970.00 -225.88 7.30 -878.10		-65.12 239.21 9.38. 290.00		207.21 11.34 327.40 1750.00		-146.00 25.01 3.01 2530.00 3900.00
1	2 Bi	+	Pbo <sub>2</sub>	п	Pb	+	2 BiO
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	208.99 9.80 271.00 1420.00 -33.78 9.64 -51.40		-66.12 239.21 9.38 290.00		207.21 11.34 327.40 1750.00		224.99
	U	+	Pb0 <sub>2</sub>	11	Pb	+	C0 <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	12.01 2.25 25.00 4347.00 -27.93 8.14 -111.18		-66.12 239.21 9.38 290.00		207.21 11.34 327.40 1750.00		-94.05 44.01 1.98 -56.20 -78.50

(cont.)	
Table 6	
Ta	

	- 1	2 DMO .	3 Pb	+ 2 La203
	4 La	4 9		-458.00
Heat of formation Molecular weight	138.92 6.15	239.21	207.21 11.34 327.40	325.84 6.51 2315.00
Density Melting point, °C	880.00	290°062	, ,	4 200 . 00
Boiling point, 'C Heat of reaction, kcal	-717.64 7.63			
$_{ m lpy}^{ m y},$	_563.60 _4299.78			
cal/			= Pb	+ 2 Li 20
	4 L1			
		-99-	10 200	29.
Heat of formation	6.94	239.21 9.38	11.34	2.01
Molecular Weight	50.00.	290.		7.001T
Density Melting point, °C	1326.00		•	
	_218.68			
2	3.44			
	-819.12			
cal/			= Pb	+ 2 MgO
	2 Mg	+ FDO <sub>2</sub>		5 7 5
		-66.12	207.21	40.
Heat of formation ,	•	239 · 21 9 · 38	11.34	3.58
Molecular werging	4/ • T	290.00	327.40	78007
point,	11 20.00		00°06/T	
Boiling point, cc	-221.56			
ν.	769,71			
<b>Q</b> , 5	-4143.65			
. 1				

Table 7

MOST ENERGETIC REACTIONS OF METALS WITH OXIDES,
IN TERMS OF VOLUMETRIC ENTHALPY

*********				Rea	cti	on				Enthalpy, _cal/cc
2	Ве	+		RuO <sub>2</sub>	=		Ru	+	2 BeO	-8279
5	Ве	+		N <sub>2</sub> O <sub>5</sub>	=	2	$N^*$	+	5 BeO	<b>-</b> 7987
7	Вe	+		Re <sub>2</sub> O <sub>7</sub>	=	2	Re	+	7 Be0	<b>-</b> 7773
4	Вe	+		RuO <sub>4</sub>	=		Ru	+	4 Be0	-7616
2	Ве	+		NO <sub>2</sub>	=		N	+	2 BeO	<del>-</del> 7390
4	Ве	+		N 204	==	2	N	+	4 Be0	-7221
2	Ве	+		so <sub>2</sub>	=		S	+	2 Be0	-6987
4	Ве	+	10		=	10	S	+	4 BeO	-6880
3	Ве	+		N 203	=	2	N	+	3 BeO	-6820
	U	+		RuO <sub>2</sub>	=		Ru	+	vo <sub>2</sub>	-6815
5	U	+	2	N2O5	=	4	N	+	5 UO 2	-6812
5	Hf	+		N <sub>2</sub> O <sub>5</sub>	=	4	N	+	5 HfO <sub>2</sub>	-6732
	Hf	+		RuO <sub>2</sub>	=		Ru	+	Hf02	-6717
2	Ве	+		Ag <sub>2</sub> O <sub>2</sub>	=	2	Ag	+	2 BeO	-6637
10	Al	+	3	N205	=	6	N	+	5 Al <sub>2</sub> O <sub>3</sub>	-6613
4	Al	+	વ	RuO <sub>2</sub>	=	3	Ru	+	2 Al <sub>2</sub> 0 <sub>3</sub>	-6571
	Hf	+		NO <sub>2</sub>	=		N	+	Hf02	-6314
5	Zr	+	2	N 205	=	4	N	+	5 ZrO <sub>2</sub>	-6266
7	U	+	2	Re <sub>2</sub> O <sub>7</sub>	=	4	Re	+	7 UO2	-6246
8	Al	+	3	RuO <sub>4</sub>	==	3	Ru	+	4 Al <sub>2</sub> 0 <sub>3</sub>	-6235
2	Вę	+		SeO <sub>2</sub>	=		Se	+	2 BeO	-6227
2	U	+		N204	=	2	N	+	2 UO <sub>2</sub>	-6221
4	Al	+	3	NO 2	=	3	N	+	2 Al <sub>2</sub> 0 <sub>3</sub>	-6206
2	Ве	+		MnO <sub>2</sub>	=		Mn		2 BeO	-6194
2	Ве	+		co <sub>2</sub>	=		C	+	2 BeO	-6185
2	Hf	+		N <sub>2</sub> O <sub>4</sub>		2	N	+	2 HfO <sub>2</sub>	-6158
7	Hf	+	2	Re 207	=	4	Re	+	7 HfO <sub>2</sub>	-6153
	Zr	+		RuO <sub>2</sub>	==		Ru	+	ZrO2	-6152
	Ве	+		ио	=		N	+	BeO	-6147
2	U	+		$RuO_4$	=		Ru	+	2 RuO <sub>2</sub>	-6435

Table 7 (cont.)

				Rea	ctio	n					Enthalpy, cal/cc
2	Be	+		PbO <sub>2</sub>	=		Рb	+	2	BeO	-6406
3	Вe	+		co203	=	2	CO	+	3	BeO	-6389
	U	+		NO <sub>2</sub>	=		N	+		vo <sub>2</sub>	-6379
2	Нf	+		RuO <sub>4</sub>	=		Ru	+	2	HfO,	-6359
5	Ве	+		As <sub>2</sub> 0 <sub>5</sub>	=	2	As	+	5	BeO	-6345
	Вe	+		CuO	=		Cu	+		Be O	-6330
4	Be-	+		Co304	=	3	Co	+	4	БеО	-6321
	Hf	+		NO <sub>2</sub>	=		N	+		HfO <sub>2</sub>	-6314
5	Zr	+	2	N205	=	4	N	+	5	ZrO <sub>2</sub>	-6266
7	U	+		Re <sub>2</sub> O <sub>7</sub>	=	4	Re	+	7	υ0 <sub>2</sub>	-6246
8	Al	+	3	RuO4	=	3	Ru	+	4	Al 203	-6235
2	Ве	+		SeO <sub>2</sub>	=		Se	*	2	ВеО	-6227
2	U	+		N204	=	2	N	+	2	υ0 <sub>2</sub>	-6221
4	Al	+	3	NO <sub>2</sub>	=	3	N	+	2	A1203	-6206
2	Вe	+		MnO <sub>2</sub>	=		Mr.	+	2	BeO	-6194
2	Be	+		co <sub>2</sub>	=		c ·	.+		BeO	-6185
2	Hf	+		N204	=	2	N	+	2	HfO <sub>2</sub>	-6158
	Be	+		NO	æ		N	+		BeO	-6147
5	Th	+	2	N2O5	=	4	14	+	5	ThO2	-6123
	Ве	+		N20	=	2	Ŋ	+		BeO	-6098
5	Ир	+	2	N205	=	4	N	+	5	NpO <sub>2</sub>	-6083
8	A1	+	3	N2O4	:@	6	N	+	4	Al 203	-6050
	Th	+		RuO	=		Кu	+		ThO <sub>2</sub>	-6003
.4	Al	+	3	Re207	=	6	Re	+	7	A1203	-5995
.0	Ti	+	3	N2O5	=	6	N	+	5	Ti <sub>2</sub> O <sub>3</sub>	-5941
3	U	<b>}</b>	2	N203	==		И	+	3	uo <sub>2</sub>	-5933
	Nр	+		RuO <sub>2</sub>			Ru	+		NpO <sub>2</sub>	-5926
	Zr	+		NO <sub>2</sub>	=		N	+		Zro <sub>2</sub>	-5902
4	В	+	3	RuO <sub>2</sub>	=	3	Ru	+	2	B <sub>2</sub> O <sub>3</sub>	-5889
2	Zr	+		RuO <sub>4</sub>	=		Ru	+	2	zro <sub>2</sub>	-5888
	Be	+		NiO	=		Ni	+		BeO	-5880
3	Hf	+	2	N203		4	И	+	3	HfO <sub>2</sub>	-5879

Table 7 (cont.)

		React	- i on				Enthalpy, cal/cc
			=	Te	+	2 BeO	-5831
2 Be	+	1602	=	N	+	ThO <sub>2</sub>	-5818
Th	<del>+</del>	2	=	Cr	+	3 BeO	-5799
3 Be	+	C103	=	Ru	+	2 ThO <sub>2</sub>	-5795
2 Th	+	$\kappa a o_4$	=	2 N	+	Al <sub>2</sub> 0 <sub>3</sub>	<b>-</b> 5780
2 Al	+	N <sub>2</sub> O <sub>3</sub>		10 S	+	2 002	<b>-</b> 5779
2 U	+	10 SO <sub>4</sub>	=	3 Ru	+	2 Ti <sub>2</sub> O <sub>3</sub>	_5757
4 Ti	+	3 RuO <sub>2</sub>	=	6 N	+	5 Ho <sub>2</sub> O <sub>3</sub>	-5751
10 Ho	+	3 N <sub>2</sub> O <sub>5</sub>	=	2 N	+	2 ZrO <sub>2</sub>	-5750
2 Zr	+	N2 <sup>O</sup> 4	=	S	+	uo <sub>2</sub>	-5749
U	+	so <sub>2</sub>	=	N	+	NpO <sub>2</sub>	5732
Ир	+	NO <sub>2</sub>	<b>*</b>	2 Ag	+	υο <sub>2</sub>	-5728
U	+	Ag <sub>2</sub> O <sub>2</sub>	=	10 S	+	2 HfO <sub>2</sub>	-5716
2 Hf	+	10 SO <sub>4</sub>	=	Ru	+	2 NpO <sub>2</sub>	-5692
2 Np	+	RuO <sub>4</sub>	, <b>32</b>	2 N	+	2 ThO 2	-5685
2 Th	+	N 2 <sup>O</sup> 4	=	S	+	HfO <sub>2</sub>	-5679
H£	+	so <sub>2</sub>	=	2 Ag	+	$HfO_2$	<b>-</b> 5676
H£	+	Ag 2 <sup>0</sup> 2	=	3 N	+	2 B <sub>2</sub> O <sub>3</sub>	-5668
4 B	+	3 NO 2	==	M	+	2 BeO	-5646
2 Be	+	WO 2	=	3 N	+	2 T1 <sub>2</sub> 0 <sub>3</sub>	-5610
4 T1	+	3 NO <sub>2</sub>	=	3 Ru	1 +	4 B <sub>2</sub> O <sub>3</sub>	-5607
8 B	+	3 RuO <sub>4</sub>	=	2 N	+	$Ta_2O_5$	-5593
2 Ta	+	N <sub>2</sub> O <sub>5</sub>	<b>=</b>	3 0	3 +	4 Al <sub>2</sub> O <sub>3</sub>	-5592
8 Al	*	3 0s0 <sub>4</sub>		3 R		2 HO <sub>2</sub> O <sub>3</sub>	<b>-</b> 5582
4 Ho		-		2 N		2 NpO <sub>2</sub>	-5576
2 Np				6 A		2 Al <sub>2</sub> O <sub>3</sub>	-5572
4 Al		3 Ag <sub>2</sub> 0 <sub>2</sub>	į.		_		-5562
7 Z:		2 Re <sub>2</sub> 0-	1				-5553
8 Ti	-	+ 3 RuO <sub>4</sub>					CC 40
10 T	-	+ 3 N <sub>2</sub> O <sub>5</sub>					5542
4 A	_	+ 3 SO <sub>2</sub>				- 3 BeO	_55 28
3 B	e	+ MoO <sub>3</sub>	Ξ	- ¥	*O		

Table 7 (cont.)

			R∈	eact:	Lon	~		Enthalpy, cal/cc
3	Zr	+	2 N <sub>2</sub> O <sub>3</sub>	=	4 N	+	3 ZrO <sub>2</sub>	-5510
7	Th	+	2 Re <sub>2</sub> O <sub>7</sub>	==	4 Re	+	$7 \text{ ThO}_2^2$	-5505
4	Но	+	3 NO <sub>2</sub>	=	3 N	+	2 Ho <sub>2</sub> O <sub>3</sub>	-5500
2	Ве	+	Mo0 <sub>2</sub>	=	Мо	+	2 BeO	-5487
8	В	+	3 N <sub>2</sub> O <sub>4</sub>	=	6 N	+	4 B <sub>2</sub> O <sub>3</sub>	-5481
3	Th	+	2 N <sub>2</sub> O <sub>3</sub>	==	4 N	+	3 ThO <sub>2</sub>	-5477
8	Ti	+	3 N <sub>2</sub> O <sub>4</sub>	=	6 N	+	4 Ti <sub>2</sub> O <sub>3</sub>	-5457
10	Sm	+	3 N <sub>2</sub> O <sub>5</sub>	=	6 N	+	5 Sm <sub>2</sub> O <sub>3</sub>	-5449
	U	+	2 NO	=	2 N	+	UO <sub>2</sub>	-5445
8	Но	+	3 RuO <sub>4</sub>	=	3 Ru	+	4 Ho <sub>2</sub> O <sub>3</sub>	-5443
10	Gđ	+	3 N <sub>2</sub> O <sub>5</sub>	=	6 N	+	5 Gd <sub>2</sub> O <sub>3</sub>	-5412
	Hf	+	2 NO	=	2 N	+	HfO <sub>2</sub>	-5406
	U	+	2 N <sub>2</sub> O	=	4 N	+	υ0 <sub>2</sub>	<b>-</b> 5395
8	Но	+	3 N <sub>2</sub> O <sub>4</sub>	=	6 N	+	4 Ho <sub>2</sub> O <sub>3</sub>	<b>-</b> 5377
10	Sc	+	3 N <sub>2</sub> O <sub>5</sub>	=	6 N	+	5 Sc <sub>2</sub> 0 <sub>3</sub>	<b>-</b> 5368
10	Nd	+	3 N <sub>2</sub> O <sub>5</sub>	=	6 N	+	5 Nd <sub>2</sub> O <sub>3</sub>	<b>-</b> 5363
	Hf	+	2 N <sub>2</sub> O	=	4 N	+	HfO2	-5357
3	Ве	+	Fe <sub>2</sub> O <sub>3</sub>	=	2 Fe	+	3 BeO	<b>-</b> 5355
4	Tb	+	3 RuO2	=	3 Ru	+	2 'Tb <sub>2</sub> 0 <sub>3</sub>	-5349
3	Np	+	2 N <sub>2</sub> O <sub>3</sub>	=	4 N	+	3 NpO <sub>2</sub>	-5348
10	La	+	3 N <sub>2</sub> O <sub>5</sub>	==	6 N	+	5 La <sub>2</sub> O <sub>3</sub>	-5339
	U	+	PbO <sub>2</sub>	==	Pb	+	vo <sub>2</sub>	-5330
2	Al	+	3 NO	==	3 N	+	A1203	-5323
4	Tb	+	3 NO <sub>2</sub>	=	3 N	+	2 Tb <sub>2</sub> O <sub>3</sub>	-5316
7	qИ	+	2 Re <sub>2</sub> O <sub>7</sub>	=	4 Re	+	7 NpO <sub>2</sub>	-5304
5	Si	+	2 N 205	=	4 N	+	5 SiO <sub>2</sub>	-5 297
	Zr	+	Ag <sub>2</sub> O <sub>2</sub>	=	2 Ag	+	Zro2	-5 297
10	Pr	+	3 N 205	=	6 N	+	5 Pr <sub>2</sub> 0 <sub>3</sub>	-5 29 3
	Th	+	Ag <sub>2</sub> O <sub>2</sub>	=	2 Ag	+	ThO <sub>2</sub>	-5 289
4	Ta	+	5 RuO <sub>2</sub>	=	5 Ru	+	2 Ta <sub>2</sub> O <sub>5</sub>	-5 284
10	Се	+	3 N <sub>2</sub> O <sub>5</sub>	3	6 N	+	5 Ce <sub>2</sub> O <sub>3</sub>	-5 276

Table 7 (cont.)

				Re	act	ion				Enthalpy, cal/cc
	Нf	+		PbO <sub>2</sub>	=		Рb	+	HEO <sub>2</sub>	-5 274
2	Al	+	3	N <sub>2</sub> 0	=	6	N	+	Al <sub>2</sub> O <sub>3</sub>	<b>-</b> 5 273
2	Zr	+	10	so <sub>4</sub>	=	10	S	+	2 ZrO <sub>2</sub>	<b>-</b> 5 266
2	Th	+		so <sub>4</sub>	=	10	s	+	2 ThO 2	-5261
4	Ta	+		NO <sub>2</sub>	=	5	N	+	2 Ta <sub>2</sub> O <sub>5</sub>	-5 25 6
2	Ti	+		N203	=	2	N	+	Ti <sub>2</sub> O <sub>3</sub>	-5 24 2
8	Tb	+	3	RuO <sub>4</sub>	=	3	Ru	+	4 Tb <sub>2</sub> O <sub>3</sub>	-5238
4	Sm	+		RuO <sub>2</sub>	=	3	Ru	+	2 Sm <sub>2</sub> O <sub>3</sub>	-5236
	U	+	2	CuO	=	2	Cu	+	υο <sub>2</sub>	-5236
	U	+		SeO <sub>2</sub>	=		Se	+	ຫວຼ	<b>-</b> 5 23 2
5	Mg	+		N205	=	2	N	+	5 MgO	-5227
4	Sm	+	3	NO <sub>2</sub>	=	3	N	+	2 Sm <sub>2</sub> O <sub>3</sub>	-5 226
2	В	+		N203	=	2	N	+	<sup>B</sup> 2 <sup>O</sup> 3	-5221
2	Но	+		N <sub>2</sub> O <sub>3</sub>	=	2	N	+	HO 203	-5206
4	Gđ	+		RuO <sub>2</sub>	=	3	Ru	+	2 Gd <sub>2</sub> 0 3	-5194
4	Gđ	+	3	NO <sub>2</sub>	=	3	N	+	2 Gd <sub>2</sub> 0 3	-5193
8	Tb	+	3	N204	2	6	N	+	4 Tb2O3	-5193
	Th	+		so <sub>2</sub>	=		S	+	ThO 2	-5188
3	U	+	2	Co203	=	4	Co	+	3 UO <sub>2</sub>	-5183
5	U	+	2	As 2 <sup>0</sup> 5	=	4	As	+	5 UO <sub>2</sub>	-5183
	Hf	+		SeO <sub>2</sub>	=		Se	+	$^{ m HfO}_2$	-5181
	Zr	+		so <sub>2</sub>	==		S	٠,	ZrO <sub>2</sub> .	-5180
	Hf	+	2	CuO	==	2	Cu	+	Hf02	-5180
2	Nb	+		N 2 <sup>O</sup> 5		2			Nb <sub>2</sub> O <sub>5</sub>	-5178
4	Nâ	+	3	NO 2	=	3	N	+	$2 \text{ Nd}_{2}\text{O}_{3}$	-5154
4	Al	+	3	PbO <sub>2</sub>	=	3	Pb	+	2 Al <sub>2</sub> 0 <sub>3</sub>	-5149
4	Nd	+		RuO 2		3	Ru	+	2 Nd 203	-5145
4	Sc	+		NO <sub>2</sub>	=	3	N	+	2 Sc <sub>2</sub> 0 <sub>3</sub>	-5144
8	Sm	+	3	RuO <sub>4</sub>	=				4 Sm <sub>2</sub> O <sub>3</sub>	-5140
4	La	+		NO <sub>2</sub>		3	N	+	2 La <sub>2</sub> 03	-5140
14	Ti	+		Re 2 <sup>O</sup> 7		6	Re	+	7 Ti <sub>2</sub> 03	-5137

Table 7 (cont.)

				Re	eact	ion					Enthalpy, cal/cc
4	Sc	+	3	RuO 2	=	3	Ru	+	2 Sc	203	-5131
8	Ta	+		RuO <sub>4</sub>	=	5	Ru	+	4 Ta		-5131
4	La	+		RuO <sub>2</sub>	=	3	Ru	+	2 La		-5128
	qN	+		Ag 202	=	2	Ag	+	фФ	$\overline{\mathfrak{s}}_2^{-}$	-5125
5	Hf	+		As 205	***	4	As	+	5 Hf	o	-5125
3	Hf	+	2	co203	· =	4	ထ	+	3 H2	$\mathfrak{d}_2^-$	-5124
2	Ве	+		GeO <sub>2</sub>	=		Ge	+	2 Be	0	-5118
	Th	+	2	NO	=	2	N	+	Th	02	-5117
14	Но	+	3	Re <sub>2</sub> 0 <sub>7</sub>	=	8	Кe	+	7 HO		-5113
	Ве	+		HgO	=		Кg	+	Ве	0	-5112
	Zr	+	2	NO	=	2	N	+	Zr	02	<del>-</del> 5105
8	Sm	+	3	N 204	=	6	Ĭ.	+	4 Sm		-5105
8	Gđ	+		RuO <sub>4</sub>	=	3	Ru	٠;٠	4 Gd		-5104
	Ŭ	+	10	so <sub>2</sub>	==	10	S	+	OU	2	<b>-</b> 5095
4	Pr	+	3	NO 2	=	3	N	+	2 Pr	2 <sup>O</sup> 3	-5093
8	Ta	+	5	N 204	==	10	N	+	4 Ta	2 <sup>O</sup> 5	-5082
4	Ce	+	3	NO <sub>2</sub>	=	3	N	+	2 Ce	203	-5074
8	Gđ	+	3	N <sub>2</sub> O <sub>4</sub>	==	6	N	+	4 Gd	203	<b>-</b> 5073
	Th	+		N <sub>2</sub> O	=	4	N	+	Th		-5072
4	Pr	+	3	RuO <sub>2</sub>	=	3	Ru	+	2 Pr	203	-5070
2	U	+		C0304	=	3	Co	+	2 UO	2	-5066
8	Nd	+	3	RuO4	=	3	Ru	+	4 Nd	203	-5063
14	В	+	3	Re <sub>2</sub> O <sub>7</sub>	=	6	Re	+	7 B <sub>2</sub>		• -5063
4	Al	+	3	SeO <sub>2</sub>	=	3	Se	+	2 Al		-5063
2	Np	+	10	so <sub>4</sub>	=	10	S	+	2 Np	02	-5061
	Zr	+	2	N 2 <sup>O</sup>	.=	4	N	+	Zr	02	-5055
8	La	+	3	RuO4	3	3	Ru	+	4 La		
2	Al	+	3	CuO	=	3	Cu		Al	203	-5051
	Hf	+		so <sub>2</sub>		10	S	+	Hf	n <sub>2</sub>	- 2046
3	Ве	+		wo 3	==		W		3 Be		-5045
4	Ce	+	3	RuO <sub>2</sub>	=	3	Ru	+	2 Ce	203	-5045

Table 7 (cont.)

	****	· · · · · · · · · · · · · · · · · · ·		R	eacti	.on			Enthalpy, cal/cc
8	Sc	+	3	$RuO_4$	=	3 Ru	+	4 Sc <sub>2</sub> 0 <sub>3</sub>	-5044
2	ďT	+		N <sub>2</sub> 0 <sub>3</sub>		2 1/1	+	Tb <sub>2</sub> O <sub>3</sub>	<b>-</b> 5036
8	Nd	+	3	N 204	.100	6 N	+	$4 \text{ Nd}_{2}^{2}\text{O}_{3}$	<b>-</b> 5036
2	Mg	+		NO <sub>2</sub>	77.	N	+	2 MgO	~5029
	U	+		$co_2^-$	~	C	+	UO <sub>2</sub>	-5028
8	La	+	3	N 2 <sup>O</sup> 4	=	6 N	+	4 La <sub>2</sub> O <sub>3</sub>	<del>-</del> 5026
4	Но	+		Ag <sub>2</sub> O <sub>2</sub>	=	6 Ag	+	2 Ho <sub>2</sub> O <sub>3</sub>	-5024
10	V	+		N 205	****	6 N	+	$5 v_{2} o_{3}$	-5020
8	Sc	+	3	N 204	=	6 N	*	4 Sc 203	-5018
4	Ti	+	3	AG2O2	=	6 Ag	+	2 Ti <sub>2</sub> 03	-5018
	Si	+		NO <sub>2</sub>	=	N	+	SiO <sub>2</sub>	-5015
2	Hf	+		Co304	=	3 Co	+	2 HfO <sub>2</sub>	<b>-</b> 5006
8	Pr	+	3	RuO <sub>4</sub>	=	3 Ru	+	4 Pr <sub>2</sub> 0 <sub>3</sub>	-4997
2	Mg	+		RuO <sub>2</sub>	Ξ	Ru	+	2 MgO	-4989
10	Al	+	3	As205	=	o As	+	5 Al <sub>2</sub> 0 <sub>3</sub>	-4988
2	Al	+		Co2O3	7	2 Co	<del>u</del> ļ.	Al <sub>2</sub> O <sub>3</sub>	-4983
8	Pr	+	3	N 204	"2	6 N	+	4 Pr <sub>2</sub> 0 <sub>3</sub>	-4978
8	Ce	+	3	RuO <sub>4</sub>	=	3 Ru	+	4 Ce <sub>2</sub> O <sub>3</sub>	-4974
	Нf	+		co <sub>2</sub>	=	C	+	$HfO_2$	-4973
	qИ	+	2	ИО	133	2 N	+	NpO <sub>2</sub>	-4964
3	Но	+	3	0504	=	3 Os	+	4 HO <sub>2</sub> O <sub>3</sub>	-4960
8	Ce	+	3	N 204	2	6 N	+	4 Ce <sub>2</sub> O <sub>3</sub> ·	-4956
2	Sm	+		N <sub>2</sub> O <sub>3</sub>	7	2 N	+	$sm_2O_3$	-4955
	ŊЭ	+		ຣບ <sub>ີ2</sub> ້	**	S	+	ν <sub>σ</sub> ος αν	-4951.
4	В	+	3	Ag 202	=	6 Ag	+	2 B <sub>2</sub> 0 <sub>3</sub>	-495%
	Si	+		RuO <sub>2</sub>	=	Ru	+	sio <sub>2</sub>	<b>-</b> 8050
3	U	`	2	so <sub>3</sub>	==	2 S	+	3 uo <sub>2</sub>	-4949

<sup>\*</sup>N refers to molecular nitrogen an is thus  $1/2 N_2$ .

Table 8

MOST ENERGETIC REACTIONS OF METALS WITH OXIDES,
IN TERMS OF GRAVIMETRIC ENTHALPY

				Re	actio	n			Enthalpy, cal/g
3	Вe	+		ио3	=	N*	+	3 3e0	-5064
5	Ве	+		N 205	=	2 N	+	5 BeO	-4703
2	Ве	+		NO <sub>2</sub>	2	N	+	2 BeO	-4686
4	Ве	+		N 204	=	2 N	+	4 BeO	-4578
3	Вe	+		N <sub>2</sub> O <sub>3</sub>	=	2 N	+	3 BeO	-4444
1	Ве	+		ИО	=	N	+	BeO	-4294
6	Li	+		й0 <sup>3</sup>	=	N	+	3 Li <sub>2</sub> 0	-4246
4	Li	+		NO <sub>2</sub>	=	N	+	2 Li <sub>2</sub> 0	-3970
10	Li	+		N <sub>2</sub> O <sub>5</sub>	==	2 N	+	5 Li <sub>2</sub> 0	-3956
8	Li	+		N20.	<b>=</b>	2 N	+	4 Li <sub>2</sub> 0	-3876
6	Li	+		N <sub>2</sub> O <sub>3</sub>	=	2 N	+	3 Li <sub>2</sub> 0	-3800
2	В	+		NO3	=	N	+	B <sub>2</sub> O <sub>3</sub>	-3765
2	Lj.	+		ИО	=	$V_{\omega}$	+	Li <sub>2</sub> 0	-3736
2	Al	+		NO3	22	N	+	Al 203	-3553
4	В	+	3	$NO_2$	==	3 14	+	<sup>2</sup> <sup>3</sup> 2 <sup>0</sup> 3	-3465
10	В	4	3	N2 <sup>O</sup> 5	=	3 N	+	5 B <sub>2</sub> O <sub>3</sub>	-3423
8	B	7		N2O4	=	6 N	+	.4 P203	-335C
4	Al	+	3	NO <sup>3</sup>	<b>=</b>	3 N	+	2.41.03	-3343
10	Al	+	3	N 205	=	6 k	+	5 A 1 203	-3309
2	1,	+		N . O3	*	2 N	+	<sup>8</sup> 2 <sup>0</sup> 3	-3297
3	Mg	· f•		NO3	===	N	+	3 Mg0	_3293
2	B	+	3	NO	===	3 N	n.f.n	B <sub>2</sub> O <sub>3</sub>	-3284
8	Al	+	3	N 2O4	ea	.6 N	+	4 Al <sub>2</sub> 0 <sub>3</sub>	-3259
	Be	+		CO	=	C	+	8e0	-3230
2	Al	+		N 203	=	2 N	+	$Al_2O_3$	-3224
??	At	4.	3	NO	≕	и Е	+	$Al_2O_3$	-3221
2	Ве	+		$co_2$	=	C	+	2 BeO	-3190
2	Вe	+		Na 2	=	Na	+	2 BeO	-3151
2	Mg			NO 2		N	+	2 MgO	-31 24

Table 8 (cont.)

			Rea	ctic	on			Enthalpy, cal/q
	Ве	+	N <sub>2</sub> O	=	2 N	+	BeO	-3120
3	Si	+	2 NO <sub>3</sub>	=	2 N		3 SiO <sub>2</sub>	-3083
4	Mg	+	N <sub>2</sub> 2 <sub>4</sub>	==	2 N	+	4 MgO	-3051
	Mg	+	NO.	=	N	+	MgO	-3045
3	Mg	+	N 203	25	2 N	+	3 MgO	-3030
	Si	+	NO <sub>2</sub>	=	11	+	${ t Sio}_2$	-2881
S	Si	+	2 N 205	=	N	+	5 SiO <sub>2</sub>	-2824
	Si	+	2 NO	=	2 N	+	$\operatorname{sio}_2^2$	-2821
2	Li	+	и 20	=	2 N	+	Li <sub>2</sub> 0	-2796
2	Sc	+	и03	=	N	+	Sc <sub>2</sub> 0 <sub>3</sub>	-2790
2	Si	+	N204	æ	2 N	+	2 SiO <sub>2</sub>	-2787
3	Si	+	2 N <sub>2</sub> O <sub>3</sub>	<b>=</b>	2 N	+	3 Sio2	-2776
2	Li	+	CO	===	C	+	Li <sub>2</sub> 0	-2769
4	Li	+	$NaO_2$	21	Na	+	2 Li <sub>2</sub> 0	-2693
2	Ве	+	so <sub>2</sub>	===	2 S	+	2 BeO	-2092
4	Sc	+	3 NO <sub>2</sub>	223	3 N	+	2 Sc <sub>2</sub> 0 <sub>3</sub>	-2662
4	Li	+	co <sub>2</sub>	=	C	+	2 Li <sub>2</sub> 0	-2657
6	Li	+	so <sub>3</sub>	=	S	*	3 Li <sub>2</sub> 0	-2650
2	St	+	3 NO	<b>3</b> 2	3 N	+	Sc₂O₃	-2644
4	Ве	+	Ru $\mathfrak{O}_{4}$	=	Ru	+	4 Be0	-2636
10	Sc	÷	3 N <sub>2</sub> O <sub>5</sub>	<b>113</b>	6 N	+	5 Sc <sub>2</sub> 0 <sub>3</sub>	-2617
5	Be	+	Mo0 <sub>5</sub>	=	Mo	+	5 BeO	2601
2	Sc	+	N 203	=	2 N	+	Sc <sub>2</sub> 0 <sub>3</sub>	-2597
3	Sc	+	$3 N_{2}O_{4}$	=	e n	+	4 Sc <sub>2</sub> 0 <sub>3</sub>	-2597
ડ	Ca	+	ио 3	=	Ñ	+	3 CaO	-2571
4	Ве	+	K204	<b>1</b>	2 K	+	♪ BeO	- 25 24
	Ca	+	ИО	=	N	+	CaO	-2475
2	Ca	+	40 S	=	N	+	2 CaO	-2471
2	Al	+	3 N <sub>2</sub> O	==	3 N	+	Al 203	-2459
	Be	+	. <b>SO</b>	=	S	+	BeO	-245.2
5	Ca	+	N <sub>2</sub> O <sub>5</sub>	⇔	2 N	+	5 CaO	-2430

Table 8 (cont.)

				React	ion						Enthalpy, cal/q
3	Ca	+		N203	=	2	N	+	3	CaO	- 24 23
4	Ca	+		N <sub>2</sub> O <sub>4</sub>	<b>12</b>	2	N	+	4	CaO	-2417
	Mg	+		и 20	=	2	N	+		MgO	<b>-</b> 2389
3	Ве	+		CrO <sub>3</sub>	=		٥r	+	3	BeO	-2358
2	В	+	3	и 20 .	=	6	N	+	1	B <sub>2</sub> O <sub>3</sub>	-2345
8	Li	+		RuO <sub>4</sub>	=		Ru	+	4	Li <sub>2</sub> O	-2339
	Ве	+		SiO	=		Si	+		BeO	-2331
4	Li	+		so <sub>2</sub>	=		S	+	2	Li <sub>2</sub> O	-2328
2	Ti	+	3	ио	=	ઉ	N	+		Ti <sub>2</sub> O <sub>3</sub>	-2323
2	Al	+	3	CO	=	3	С	+		Al <sub>2</sub> O <sub>3</sub>	-2318
4	Ti	+	3	NO2	=	6	N	+	2	Ti <sub>2</sub> O <sub>3</sub>	-2300
4	Ве	+		Nb <sub>2</sub> O <sub>4</sub>	=	2	ИÞ	+		BeO	<del>-</del> 2284
2	P	+		ио3	=		N	+		P <sub>2</sub> O <sub>3</sub>	-2282
10	Li	+		MoO <sub>5</sub>	=		Мо	+	5	Li <sub>2</sub> 0	-2269
2	Ti	+		N <sub>2</sub> O <sub>3</sub>	=	2	N	+		Ti <sub>2</sub> O <sub>3</sub>	-2252
10	Ti	+	3	N <sub>2</sub> O <sub>5</sub>	===	6	N	+	5	Ti <sub>2</sub> 0 <sub>3</sub>	-2247
4	Лl	+		NaO <sub>2</sub>	=	3	Na	<b>-</b> }-		Al <sub>2</sub> O <sub>3</sub>	-2244
	Mg	+		co	=		С	+		MgO	-2244
8	Ti	+	3	$N_2O_4$	=	6	N	+	4	Ti <sub>2</sub> O <sub>3</sub>	-2237
8	Li	+		K <sub>2</sub> O <sub>4</sub>	=	2	K	+		Li <sub>2</sub> 0	-2203
2	P	+	3	ио .	=	3	N	+		P203	-2202
2	Li	+		so	=	•	s	+		Li <sub>2</sub> o	-2201
2	Al	+		so <sub>3</sub>	=		S	+		Al <sub>2</sub> O <sub>3</sub>	-2197
2	Ве	+		Li <sub>2</sub> O <sub>2</sub>	=	2	Li	+		BeO	-21.95
2	Mg	+		NaO <sub>2</sub>			Na	+	2	MgO	-2178
4	P	+					N	+	2	P 203	
4	Al	+		CO <sub>2</sub>		3	С	+	2	A1203	-2150
3	Mg	+		so <sub>3</sub>				+		MgO	
2	S¢	+	3	и20	=	6				Sc 203	
2	В	+		co						B <sub>2</sub> O <sub>3</sub>	
	Si	+		N 20				+		sio <sub>2</sub>	-2104
				-						<i>i</i> .	

Table 8 (cont.)

				Rea	ctio	on_					Enthalpy, cal/q
2	P	+	N	12 <sup>0</sup> 3	=	2	N	+		P 2 <sup>O</sup> 3	-2101
4	Ве	+		1004	=		Мо	+	4	BeO	-2094
2	Mg	+	C	2	=		С	+	2	MgO	-2089
10	P	۳ir		12 <sup>0</sup> 3	=	ō	N	+	5	P <sub>2</sub> O <sub>3</sub>	-2082
8	P	+		204	=	6	N	+		P <sub>2</sub> O <sub>3</sub>	-2075
2	Li	+	S	iO	=		Si	+		Li <sub>2</sub> O	-2073
3	Ве	+	K	203	=	2	K	+	3	BeO	-2042
6	I.i	+		203	=		Cr	+	3	Li <sub>2</sub> 0	-2038
	Са	+	N	20	=	2	N	+		CaO	-2037
7	Ве	+	r	1° 2° 7	=	2	Tc	+	7	BeO	-2026
8	Al	+	3 F	lu0 <sub>4</sub>	=	3	Ru	+	4	Al <sub>2</sub> O <sub>3</sub>	-2020
3	Zr	+	2 N	10 <sub>3</sub>	=	?	N	+	3	ZrO2	-2013
4	В	. +	3 N	la02	<b>25</b>	3	Na	+	2	B <sub>2</sub> O <sub>3</sub>	-2008
	Zr	+	2 N		=	2	N	+		ZrO <sub>2</sub>	-1992
4	Mg	+		\u0_4	=		Ru	+	4	MgO	-1990
4	Al	+	3 8	so <sub>2</sub>	==	3	S	+	2	Al <sub>2</sub> O <sub>3</sub>	-1950
2	B	+	S	so <sub>3</sub>	=		S	+		B <sub>2</sub> O <sub>3</sub>	-1940
	Zr	+		102	=		N	+		Zro2	-1940
3	C	+	2 N	103	<b>25</b>	2	N	+	3	CO <sub>2</sub>	-1925
2	Ве	+	M	1g0 <sub>2</sub>	***		Mg	+	2	BeO	-1924
2	Al	+	3 5	SO	=	3	s	+		Al <sub>2</sub> O <sub>3</sub>	-1923
2	Mg	+	9	<sup>2</sup>	=		S	+	2	MgO	-1922
10	Al	7	4 6	1005	=	3	Мо	+	5	Al 2 <sup>0</sup> 3	_1918
3	Zr	+		1202	==	4	N	*	3	zro <sub>2</sub>	-1913
2	Sc	+	3 C	0.0	22	3	C	+		Sc 203	-1907
	C	۲	2 1	10	=	2	N	+		co <sub>2</sub>	-1905
	Mg	÷	S	<b>5</b> 0	=		S	+		MgO	-1904
5	Mg	+	1	1005	=		Мо	+	5	MgO	-1895
2	Zr	*	1	1204	m	2	N	+	2	zro <sub>2</sub>	-1890
5	Zr	+		1 <sub>2</sub> C <sub>5</sub>		4	N	+	5	2ro2	-1890
3	Ti	+		103	<u>m</u>		N	+	3	TiO	-1.870
2	Ti	+		1 2 C	=	6	N	÷		Ti <sub>2</sub> O <sub>3</sub>	-1867

				Read	ctio	n				Enthalpy, _cal/g
5	Be	+		As 2 <sup>0</sup> 5	=	2 .	As	+	5 BeO	-1860
8	Al	+	3	K <sub>2</sub> O <sub>4</sub>	=	6	K	+	4 Al <sub>2</sub> 0 <sub>3</sub>	-1859
2	V	+		ИО	=	3	N	+	v <sub>2</sub> 0 <sub>3</sub>	-1848
2	V	+		ио3	=	1	N	+	$v_2^{-0}$	-1848
4	Sc	+	3	NaO <sub>2</sub>	=	3	Na	+	2 Sc <sub>2</sub> 0 <sub>3</sub>	-1845
	Ca	+		CO .	=	•	C	+	CaO	-1843
4	Mg	+		K204	=	2	K	+	4 MgO	-1842
8	Li	+		M00 <sub>4</sub>	=		Mo	+	4 Li <sub>2</sub> 0	-1838
4	В	+	3	co <sub>2</sub>	==	3	C	+	2 B <sub>2</sub> O <sub>3</sub>	-1835
2	Ве	+		SeO <sub>2</sub>	=		Se	+	2 BeO	-1826
	Si	+	2	co	=	2	C	+	SiO <sub>2</sub>	-1814
8	В	+	3	RuO <sub>4</sub>	=	3	Ru	+	4 B <sub>2</sub> O <sub>3</sub>	-1802
2	Sc	+		so <sub>3</sub>	<b>=</b>		S	+	Sc <sub>2</sub> 0 <sub>3</sub>	-1802
6	Li	+		к203	=	2	K	+	3 Li <sub>2</sub> 0	-1800
14	Li	+		Tc 207	=		Tc	+	7 Li <sub>2</sub> 0	-1794
2	Ca	+		NaO <sub>2</sub>	=		ьИ.	+	2 Ca0	-1789
2	Al	+	3	SiO	=	3	Si	+	Al <sub>2</sub> O <sub>3</sub>	<b>-</b> 1785
2	Ве	+		$Na_2O_2$	=	2	БЙ	+	2 BeO	-1785
8	Be	+		Re <sub>2</sub> C <sub>8</sub>	=	2	Re	+	8 BeC	-1780
	Mg	+		SiO	=		Si	+	MgO	-1778
3	Be	+		TcO3	=		TC	+	3 BeO	-1775
4	V	+	3	NO <sub>2</sub>	<b>=</b>	3	N	+	2 v <sub>2</sub> 0 <sub>3</sub>	-1767
	C	+		NO 2	==		N	+	co <sub>2</sub>	-1760
3	Ca	+		so <sub>3</sub>	=		S	÷	3 CaO	1752
2	V	+		$N_2 \Omega_3$	===	2	N	+	$v_2o_3$	-1742
8	Sc	Ŧ	3	$RuO_4$	as.	,3	Ru	+	4 Sc <sub>2</sub> 0 <sub>3</sub>	-1736
4	Sc	+	3	co <sub>2</sub>	azo	3	C	+	2 Sc <sub>2</sub> O <sub>3</sub>	-1731
8	Li	+		Nb204	278	2	Nb	+	4 Li <sub>2</sub> O	-1725
2	Cr	+	3	ИО	=	3	N	+	Cr <sub>2</sub> O <sub>3</sub>	-1723
2	B	+	3	SO	<b>33</b> 5	3	S	+	B <sub>2</sub> O <sub>3</sub>	-1712
	C		2	N 203	ida.	4	N	+	3 co <sub>2</sub>	-1712
8	<b>A</b>	*	ڏ	N204	<u> </u>	б	N	+	4 V <sub>2</sub> 0 <sub>3</sub>	-1707
4	⊋a_	+		RuO4	=		Ru	+	4 Ca0	-1704

Table 8 (cont.)

_				React:	ion					Enthalpy, cal/g
10	V	+	3	N2 <sup>O</sup> 5	<b>'</b>	6	И	+	5 V <sub>2</sub> O <sub>3</sub>	-1703
2	Cr	+		ио3	==		И	+	cr <sub>2</sub> 0 <sub>3</sub>	-1702
2	Nb	+	5	ио	=	5	N	+	Nb <sub>2</sub> O <sub>5</sub>	-1700
	Ве	+		InO	=		In	+	BeO	-1695
3	Mg	+		cro3	=		Cr	+	3 MgO	-1694
2	P	+	3	N20	æ	6	N	4-	P203	-1693
2	Al	+		cro <sub>3</sub>	=		Cr	+	Al <sub>2</sub> 0 <sub>3</sub>	-1693
4	Be	+		0504	=		0s	+	4 BeO	-1690
4	Be	+		$Rb_2\hat{O_4}$	=	2	Rb	+	4 BeO	-1689
2	Ca	+		co <sub>2</sub>	=		C	+	2 CaO	-1689
2	Sc	+	3	ຣ໐້	<b>278</b>	3	S	+	Sc203	-1678
6	Nb	+	5	ио3	=	5	N	+	3 Nb <sub>2</sub> 0 <sub>5</sub>	-1676
3	Si	+	2	so <sub>3</sub>	=	2	S	+	3 SiO <sub>2</sub>	-1665
4	В	+	3	so <sub>2</sub>	=	3	S	+	2 B <sub>2</sub> O <sub>3</sub>	-1661
	Zr	+	2	N <sub>2</sub> O	=	4	N	+	zro <sub>2</sub>	-1657
	Ca	+		so	==		s	+	CaO	-1655
10	Li	+		As 205	=	2	As	+	5 Li <sub>2</sub> 0	-1649
4	Li	+		SeO <sub>2</sub>	=		Se	+	2 Li <sub>2</sub> 0	-1646
10	В	+	3	MoOs	=	3	Мо	+	5 B <sub>2</sub> O <sub>3</sub>	-1642
2	Ç	+		N2O4	<b>a</b>	2	N	+	2 CO <sub>2</sub>	-1641
4	Sc	+	3	so <sub>2</sub>	==	3	S	+	2 Sc <sub>2</sub> 0 <sub>3</sub>	-1637
5	C	+	_		. = <u>.</u>	4	N	+	5 CO <sub>2</sub>	-1630
4	Cr	+	3	NO 2	==	3	N	+	2 Cr <sub>2</sub> O <sub>3</sub>	-1628
10	Sc	+	3	MoO <sub>5</sub>	==	3	Мо	+	5 Sc <sub>2</sub> 0 <sub>3</sub>	-1626
16	Li	+		Re <sub>2</sub> O <sub>8</sub>	===	2	Re	+	8 Li <sub>2</sub> 0	-1620
2	Si	*		RuO <sub>4</sub>	223		Ru	+	2 SiO <sub>2</sub>	-1617
4	Li	+		MgO <sub>2</sub>	=		Mg	+	2 Li <sub>2</sub> 0	-1616
2	Са	+		so <sub>2</sub>	===		S	+	2 Ca0	-1614
2	Li	+		InO	##		In	+	Li <sub>2</sub> 0	-1613
2	Cr	+		N 2 <sup>O</sup> 3	=	2	N	+	Cr <sub>2</sub> O <sub>3</sub>	-1609
4	Ир	+	5	NO <sub>2</sub>	=	5	N	+	2 Nb <sub>2</sub> O <sub>5</sub>	-1606
5	Ca	+		M005	==		Mo	+	5 CaO	-1605
2	ΙT	+	3	CO	==	3	С	+	Ti <sub>2</sub> 03	-1600
2	Ве	+		$^{MnO}_2$	=		Mn	+	2 BeO	-1595
6	Nb	<b>4.</b>	5	N 2 <sup>O</sup> 3	=	10	N	+	3 Nb <sub>2</sub> O <sub>5</sub>	-1588

<sup>\*</sup>Refers to molecular nitrogen and is thus  $1/2 N_2$ .

The oxides of nitrogen are excellent oxidizers because they uniquely combine the characteristics of a slightly positive heat of formation, a small gram-atomic volume, and small values of z and y in their stoichiometric equations. In addition to the unusually large thermal outputs, their reactions are unique in other respects. For instance, with many metals either gaseous nitrogen or a metal nitride is produced:

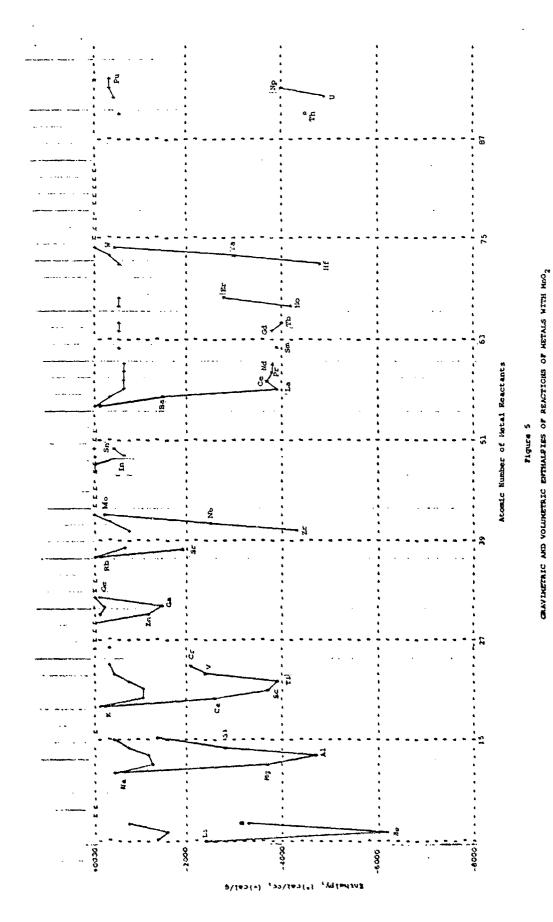
Be + 
$$1/4 \text{ N}_2\text{O}_4 \longrightarrow 1/4 \text{ N}_2 + \text{BeO}$$
  
 $7/4 \text{ Be} + 1/4 \text{ N}_2\text{O}_4 \longrightarrow 1/4 \text{ Be}_3\text{N}_2 + \text{BeO}$ 

Only the reactions producing gaseous nitrogen were considered here.

The periodicity of the enthalpies is illustrated in Figures 5, 6, and 7. The periodic behavior demonstrated by the oxides is somewhat different from that of the fluorides. Energy peaks (actually minima in the curves) occur at every ninth atomic number, forming the series beryllium, aluminum, titanium, gallium, zirconium, indium, and hafnium. Except for beryllium, these elements comprise Groups IIIA and IVB. In this analysis the elements from lanthanum to lutetium are considered as one The rare earth elements, lanthanum to holmium and probably thorium to element 103, also form a broad energy peak within the peaks separated by nine units. The elements at the energy peaks are characterized by the electronic configuration of their valence orbitals. The electronic configuration in the oxides is the rare gas so or spoor the pseudo rare gas s<sup>2</sup>p<sup>6</sup>d<sup>10</sup>. Other characterizing features of the energy peaks are the high heats of formation of their oxides relative to the oxides of their immediate neighbors, their low gram-atomic volumes, and their low values of z and y due to the stoichiometry of their oxidation states.

The high volumetric energy outputs exhibited by the reactions with beryllium are due to the extremely low atomic volume of the metal. It also exhibits a high gravimetric energy output because its atomic weight is low. Because of these factors, the heat of formation of the oxide per unit volume and per unit weight is comparatively high. The heat of formation of magnesium oxide is about the same as that of beryllium oxide, but the atomic volume and the atomic weight of the metal are greater. Magnesium reactions are therefore not as energetic as beryllium reactions.

A similar situation exists between boron and aluminum. The smaller atomic volume and atomic weight of boron tend to increase the volumetric and gravimetric energies of its reactions. But aluminum reactions are much more energetic because aluminum oxide has a much higher heat of formation than boric oxide. These factors are discussed more thoroughly under nitrate reactions.



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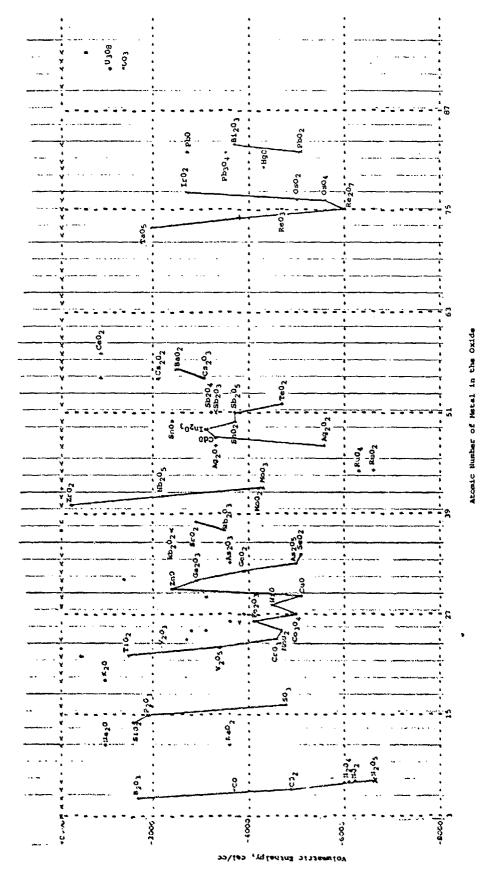
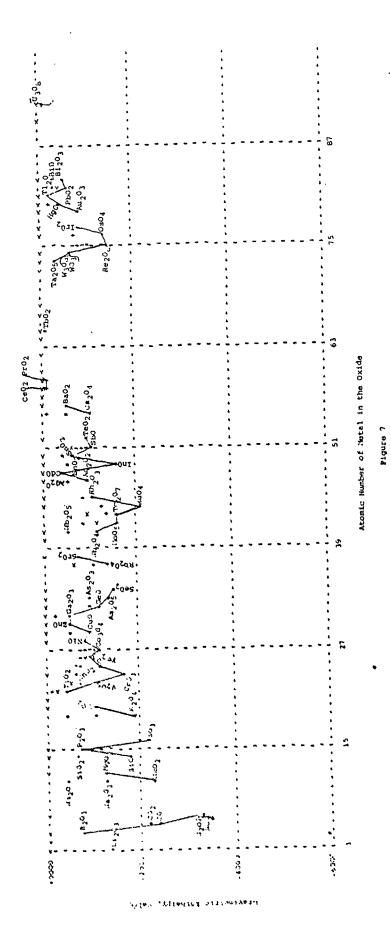


Figure 6 WOLUNGTRIC ENTHALPIES OF REACTIONS OF OXIDES WITH AL

51



ASD-TDR-63-846

Titanium, zirconium, and hafnium occupy peak positions because their gram-atomic volumes are relatively low and the heats of formation of their oxides are relatively high. Although gallium and indium have very low energy outputs, they are higher than their immediate neighbors because of their lower gram-atomic volumes and because of the higher heats of formation of their oxides relative to those of their neighbors. The extremely low gram-atomic volume of beryllium placed it in a peak position, in spite of the relatively low heat of formation of its oxide.

The peak positions of the rare earths lanthanum to holmium are due to the reverse phenomenon. Their relatively large gram-atomic volumes are compensated by the extremely high heats of formation of their oxides. Although data are not available, it seems that the energy outputs of all the members of the rare earth series should be comparable and therefore they will establish a horizontal position in the curve between lanthanum and lutetium. The Volumetric energy for erbium is based on a questionable value for the density of the metal--4.77 g/cc. The anomalous position it occupies in the volumetric curve indicates that this density is probably in error. The interposition of the rare earth elements between zirconium and hafnium plus the lanthanide contraction cause hafnium to have a gram-atomic value comparable to that of zirconium even though its atomic weight is much greater.

The trend of the enthalpies within the various groups of the periodic table is similar to that of the fluorides (Figure 1B). The energy decreases from lithium to cesium. Group IIA energies also decrease from beryllium to barium. The Group II values are higher than the Group I values because all the factors —  $\Delta H_{AO_X}$ , gram-atomic volume, z, and y — are more favorable. Group III elements exhibit a similar trend, but their outputs are lower, because the less favorable z and y values predominate even though their  $\Delta H_{AO_X}$  is and gram-atomic volumes are more favorable. This relationship is best illustrated by comparing calcium and gallium, which have gram-atomic volumes of 25.8 and 11.8 cc and  $\Delta H_{AO_X}$  is of 152 and 259 kcal, respectively. In spite of these decided advantages, the thermal release of calcium is superior to that of gallium because of the more favorable z and y values. Because of the unusually high heat of formation of its oxide, aluminum occupies an anomalous position above magnesium.

The trend in enthalpies within the transition metal groups in the periodic table is also similar to that of the fluorides (Figure 1C). The first two groups, copper, silver, gold,\* and zinc, cadmium, mercury, exhibit a decrease in enthalpy with

Copper, silver, and gold are not shown on the plot in Figure 5 because their reactions yield positive enthalpies.

increasing atomic number. Their enthalpies are all very low because of their low  $^{\Delta}\text{H}_{AO_{\chi}}$ 's. The energies decrease both because the  $^{\Delta}\text{H}_{AO_{\chi}}$ 's decrease and because the gram-atomic volumes increase with increasing atomic number.

Within Group IVB (titanium, zirconium, and hafnium), Group VB (vanadium, niobium, and tantalum,) and Group VIB (chromium, molybdenum, and tungsten) the enthalpies increase with atomic number because their gram-atomic volumes and the heats of formation of their exides become more favorable. In comparing one group with another, however, the normalized enthalpies decrease with increasing group number. The reasons for this differ between Groups IV and V and between Groups V and VI. Even though the gram-atomic volumes and  $\Delta H_{AO}$  's of Group V are nore favorable than those of Group IV, their energies are lower because of the predominant effect of the unfavorable z and y values. Whereas the gram-atomic volumes and the z and y values of Group VI are more favorable, the unfavorable  $\Delta H_{AO}$  's cause Group VI energies to be even lower than those of Group'V.

Curves of the type shown in Figure 5 were drawn for the other oxides. Similar trends were exhibited, but the curves were displaced vertically because of the differences in the parameters of each oxide.

The volumetric and gravimetric enthalpies of the reactions of the various oxides with aluminum metal are shown in Figures 6 and 7, respectively. These curves appear as an inverted version of the curves in Figure 5 because the metals that act as effective reducing agents form oxides that are poor oxidizing agents and vice versa. Thus the maximum volumetric energy outputs occur with the oxides of nitrogen, arsenic, sulfur, selenium, tellurium, the transition metals (chromium, manganese, iron, cobalt, nickel, copper, molybdenum, ruthenium, silver, rhenium, and osmium and lead. The gravimetric behavior is similar, with the notable exception of the alkalı metals. They exhibit relatively high gravimetric outputs, but their volumetric outputs are relatively low because of their very low densities. These curves enable one to determine the best oxide that can be used with aluminum metal for applications involving different parameters. Similar curves were drawn for all the metals.

The volumetric and gravimetric enthalpies of 9636 reactions of the oxides are summarized in Tables 9 and 10, respectively. The most energetic reactions are in the upper left portion of the tables. The most effective oxidizers are on the left and the most effective reducing agents are on the top. The orders of efficacy mentioned previously are confirmed here.

Table 9

VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH OXIDES (In descending order from top to bottom and left to right)

8	1665-	6161	-4707	-4588	6847-	-4278	-4172	-4353	-4C72	240.83	14050	1000	-4500	- 1940	-3440	3750	6145	1695	975/-	-¥158	-2657	1123	1000	-2540	12098	-2697	-2160	1641	*1568		- E 17	-1150	657-	11446	-2233	141	-967	213	11053	-176	205	1000	270	165	ì	459	1745	-263	-350	00 a	1
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## C. Nitrate and Nitrite Reactions

The interactions of 18 nitrates and 8 nitrites with metals were examined, and 1226 reactions resulted. The groups of reactions embodying the nitrates and nitrites are highly energetic. In general, the nitrates are more energetic than the nitrites.

The data for a few of the more energetic reactions are shown in Table 11. These data were abstracted from the series of reactions of elements with lead nitrate listed on the computer data sheets. Reactions with lead nitrate can produce several oxides. For aluminum, boron, beryllium, calcium, and cesium, the most energetic reaction produces Pb<sub>2</sub>O. For barium, bismuth, carbon, and cadmium, the most energetic reaction produces PbO. The reactions producing Pb<sub>2</sub>O are generally more energetic.

Table 12 lists the 199 most energetic nitrate and nitrite reactions. Beryllium, uranium, hafnium, aluminum, zirconium, thorium, boron, titanium, tantalum, neodymium, lanthanum, scandium, praseodymium, cerium, magnesium silicon, vanadium, chromium, niobium, gallium, and calcium are the best reducing metals, in that order. Lithium nitrate, lead nitrate, calcium nitrate, strontium nitrate, silver nitrate, sodium nitrate, barium nitrate, potassium nitrate, rubidium nitrate, barium nitrite, silver nitrite, sodium nitrite, and cesium nitrate are the best oxidizing agents, in that order. These relationships are depicted graphically in Figures 8, 9, and 10.

The periodicity of the data is apparent in Figure 8. These curves are similar to those depicting the behavior of oxides with metals, and the same rules seem to be applicable. The "rule of nine" that was observed in the oxide reactions is still valid: the minima in the curve, corresponding to maximum thermal outputs, occur at every ninth atomic number starting with beryllium, aluminum, titanium, gallium, zirconium, indium (no data), lanthanum, and hafnium.

The dotted lines connect the members of a periodic group with five or more members. Thus, the members of Groups IA (lithium, sodium, potassium, rubidium, and cesium) and IIA (beryllium, magnesium, calcium, strontium, and barium) are connected. The energy of the reaction decreases with increasing atomic number of the members of a group. This is generally true for the other "long" groups (IIIA and VIA), except for anomalies evident at aluminum and carbon.

These anomalies are related to the volumetric enthalpy, which is highly dependent upon the heats of formation of the products and reactants, on the volume of the reactants, and on the coefficients of the terms in the balanced equation. Aluminum and boron have the same stoichiometric coefficients, and

Table 11

DATA ON REACTIONS OF VARIOUS METALS WITH LEAD NITRATE

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point, oc	23.27.			•	i i
Heat of reaction, kcal	9 W W				
Reactants' density Gravimetric enthalpy, cal/g	1501.88 .5922.77	!			
Į.	22 B +	6 Pb(NO <sub>3</sub> ) <sub>2</sub>	$= 3 \text{ Pb}_2 \text{O} +$	11 B <sub>2</sub> 0 <sub>3</sub>	+ 6 N <sub>2</sub>
		,35	9	-302,00	00 80
Heat of formation	ω	331, 23			ų.
MOLECULAL WELGING	ຜ	4,	υ	٠ ١	g
Density Melting point, °C	0,0	470.00		, •	195
	2550.00				
Reactants density	٦, ۱				
Gravimetric enthalpy, cal/g	مع <i>ل</i> ه				
1	5 Ba +	Pb(NO <sub>3</sub> ) <sub>2</sub>	= Pb0	+ 5 BaO	+ N <sub>2</sub>
ļ	de se se s'estado de section de s	07,35	52.	4	
Heat of formation		331	223,21 8,00		28.02
Density		υ <sup>°</sup> O	,	0	. 209,86
		ı		00.00	.ck1
Boiling Point, Wal					
•	601 777				
<b>\</b> 1	7 7				

Table 11 (cont.)

	11 Be +	$+ 2 \text{ Pb (NO}_3)_2 =$	Pb20 +	11 BeO +	2 N <sub>2</sub>
Heat of formation Molecular weight	3	35	-51.20 430.42	-146.00 25.01	28.02
Density Melting point, °C	1.85 1283.00	က္	M 3	၁၀၀	-209.86
	ő ;			ວຸດ	ດໍ
s density	, n				
Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc	4 4				
	10 Bi +	+ 3 Pb (NO <sub>3</sub> ) $_2 =$	3 Pb0 +	$5 \text{ Bi}_{203} +$	3 N <sub>2</sub>
Heat of formation		07.3	v	3	•
Ø	3	31	223.21 8.00	466.00	28.02
Density Molting mother of	, [ ]	j Ö	Q		-209.85
point,	20.			90.	•
Heat of reaction, kcal					
Reactailts usisity Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc					
	5 5	$+ 2 Pb(NO_3)_2 =$	: 2 PbO +	5 co <sub>2</sub> +	2 N <sub>2</sub>
Heat of formation		07.3	52.	0,	
- 171	ی	7	223.21	4.0	28.02
1	ď,		٥	0,4 0,4	o c
	25.00	Ş		-78.50	195.80
Bolling Point, C Heat of reaction, Kcal	360.				
	4				
Gravimetric enthalpy, cal/g Volumetric enthalply. cal/cc	-498.74 -2083.80				
4					

Table 11 (cont.)

	11 Ca +	$2 \text{ Pb (NO}_3)_2 =$	Pb <sub>2</sub> 0	+ 11 CaO +	$2 N_2$
Heat of formation	1	35	-51.20 430.42	တ်ဝိပ	28.02
Density Melting point, °C Boiling point, °C	1,55 850,00 1240,00	ကို ဝ	 	3,33 2580,00 2850,00	209.86 -195.80
Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/c	տ այա	•		to the game of the second of t	
and the control of th	5 Cd +	Pb $(NO_3)_2 =$	Pbo	+ 5 CdO +	+ N <sub>2</sub>
Heat of formation	4	-107,35 331,23	_52.40 223.21	_60 86 128.41	28,02
Folecaid words: Density Molting notet °C	8,6	က် ဝ	0	٠,0	. 209,86
Boiling point, "C Heat of reaction, kcal	٥٠٠٠				0 7 6 6 7
Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc	6.47 279.14 -1804.64				
•	22 Ce +	$6 \text{ Pb (NO}_3)_2 =$	3 Pb20	$+11 \text{ Ce}_{203} +$	6 N <sub>2</sub>
Base of formation		, 35	51.2	000	(
ď	_		430.42	328 26 6 90	28.02
Density Melting point, 'C	775,00	0		0	209,86
	2900.00 4294.50				) ; ) )
	ഗ				
Gravimetric unthalpy, cal/g Volumetric enthalpy, cal/cc	ט נ				
elitario, and allega capital calls during the call of the same of					

Table 12

MOST ENERGETIC NITRATE AND NITRITE REACTIONS WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

					R	eaction						Enthalpy, cai/cc
5	Ве	+	2	Li(NO <sub>3</sub> )	=	Li <sub>2</sub> 0	+	5	BeO	+	N <sub>2</sub>	-7798
11	Ве	+	2	Pb(NO <sub>3</sub> ) <sub>2</sub>	=	Pb <sub>2</sub> O	+	11	BeO	+	2 N <sub>2</sub>	-7218
5	Ве	+		$Ca(NO_3)_2$	=	CaO	+	5	BeO	+	$^{\rm N}_2$	<del>-</del> 7006
5	Ве	+		$Sr(NO_3)_2$	=	Sr0	+	5	BeO	+	N <sub>2</sub>	<b>-</b> 6697
5	Ве	+	2	Ag(NO <sub>3</sub> )	=	Ag <sub>2</sub> O	+	5	BeO	+	N <sub>2</sub>	-6623
5	U	+	4	Li(NO3)	=	2 Li <sub>2</sub> 0	+	5	υ0 <sub>2</sub>	+	2 N <sub>2</sub>	-6537
5	Hf	+	4	Li(NO <sub>3</sub> )	=	2 Li <sub>2</sub> 0	+	5	HfO <sub>2</sub>	+	2 N <sub>2</sub>	-6454
10	Al	+	6	Lj (NO3)	= ,	3 Li <sub>2</sub> 0	+	5	Al <sub>2</sub> 0 <sub>3</sub>	+	3 N <sub>2</sub>	-6324
11	U	+	4	Pb(NO3) 2	=	2 Pb <sub>2</sub> O	+	11	UO2	+	4 N <sub>2</sub>	-6110
5	Be	+	2	иа (NO <sub>3</sub> )	==	Na <sub>2</sub> O	+	5	BeO	+	N <sub>2</sub>	-6090
11	нf	+	4	Pb(NO3/2	=	2 Pb <sub>2</sub> O	+	11	HfO2	+	4 N <sub>2</sub>	-6042
5	Вę	+		Ba (NO3) 2	=	BaO	+	5	BeO	+	N <sub>2</sub>	<b>-</b> 5963
5	Zr	+	4	Li(NO3)	<b>=</b>	2 Li <sub>2</sub> 0	+	5	ZrO2	+	2 N 2	<del>-</del> 5956
5	U	+	2	$Ca(NO_3)_2$	=	2 CaO	+	5	UO <sub>2</sub>	+	2 N <sub>2</sub>	-5948
22	Al	+	3	Pb(NO <sub>3</sub> ) <sub>2</sub>	<b>=</b>	3 Pb <sub>2</sub> 0	+	11	A1203	+	6 N <sub>2</sub>	-5922
5	Hf	+	2	$Ca(NO_3)_2$	=	2 CaO	+		$^{\rm HfO}_2$	+	2 N <sub>2</sub>	-5884
5	Th	÷	4	Li(NO <sub>3</sub> )	=	2 Lt <sub>2</sub> 0	+		ThO <sub>2</sub>	+	2 N <sub>2</sub>	-5849
10	Al	+	3	$Ca(NO_3)_2$	za	3 CaO	÷	5	VT 503	+	3 N <sub>2</sub>	<b>-5767</b>
10	В	+	6	r; (no3)	=	3 Li <sub>2</sub> 0	+	5	B <sub>2</sub> O <sub>3</sub>	+	°N <sub>2</sub>	-5674
5	U	+	2	$sr(NO_3)_2$	=	2 SrO	+	5	$w_3$	+	2 N <sub>2</sub>	-5674
5	U	+		$Ag(NO_3)$	=	2 Ag <sub>2</sub> O	+		$uo_2$	+	2 N <sub>2</sub>	-567.2
5	Hf	+		$Ag(NO_3)$	=	2 Ag <sub>2</sub> O	+	5	$HfO_2$	+	2 N <sub>2</sub>	-5618
5	Hf	+	2	$Sr(NO_3)_2$	=	2 Sr0	+	5	HfO <sub>2</sub>	+	2 N <sub>2</sub>	-5616
10	Ti	+		T7 (NO <sup>3</sup> )		3 L1 <sub>2</sub> 0	+			+	3 N <sub>2</sub>	-5603
11	Zr	+	4	Pb(NO <sub>3</sub> ) <sub>2</sub>	=	2 Pb <sub>2</sub> O	+	11	$z_{r0}_2$	+	4 N <sub>2</sub>	-5594
11	Th	+	4	$Pb(NO_3)_2$	to.	2 Pb <sub>2</sub> 0	÷	11	ThO 2	+	4 N <sub>2</sub>	-5544
10	Al	+	6	Ag (NO <sub>3</sub> )	<b>=</b>	3 Ag <sub>2</sub> 0	+	5	A1 203	+	3 N <sub>2</sub>	-5510
				$sr(NO_3)_2$		3 Sr0					3 N <sub>2</sub>	-5500
5	Zr	*	2	Ca (NO <sub>3</sub> ) 2	=	2 CaO	+	5	2r0 <sub>2</sub>	+	$2N_2$	-5452

Table 12 (cont.)

							React	ion					Enthalpy, cal/cc
5	Th	+	2	$Ca(NO_3)_2$	=	2	CaO	+	5	ThO <sub>2</sub>	+	2 N <sub>2</sub>	-5422
22	Ti	+	6	Pb(NO <sub>3</sub> ) <sub>2</sub>	=	3	C_dq			T1203		6 N <sub>2</sub>	-5 270
22	В	+	6	$Pb(NO_3)_2$	=	3	⊃b <sub>2</sub> 0			B <sub>2</sub> O <sub>3</sub>	+	5 N <sub>2</sub>	-5 251
5	Th	+	4	Ag(NO3)	=		Ag <sub>2</sub> O	+	5	ThO <sub>2</sub>	+	2 N <sub>2</sub>	~5 224
5	Zr	+	4	$Ag(NO_3)$	=	2	Ag <sub>2</sub> 0	+	5	ZrO2	+	2 N <sub>2</sub>	-5 223
5	Th	+	2	$Sr(NO_3)_2$	=	2	SrO	+	5	ThO <sub>2</sub>	+	2 iJ <sub>2</sub>	-5199
5	Zr	+	2	$Sr(NO_3)_2$	=	2	SrO	+	5	ZrO <sub>2</sub>	+	2 N 2	-5195
5	Ta	+	2	Li(NO <sub>3</sub> )	=		Li <sub>2</sub> 0	+		Ta205	+	N <sub>2</sub>	<b>-</b> 5103
5	J	+	4	$Na(NO_3)$	=	2	Na <sub>2</sub> 0	+	5	UO 2	+	2 N <sub>2</sub>	-5151
10	Τi	+	3	Ca(NO <sub>3</sub> ) <sub>2</sub>	=	3	CaO	+	5	Ti <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-5137
5	Ħf	+	4	$Na(NO_3)$	==	2	Na <sub>2</sub> O	+	5	$HfO_2$	+	2 N <sub>2</sub>	-5104
10	₿	+	3	$Ca(NO_3)_2$	=	3	CaO	+	5	B <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-5088
10	Nd	+	6	Li(NO3)	<b>:</b>	3	Li <sub>2</sub> 0	+	5	Nd 203	+	3 N <sub>2</sub>	-5080
5	U	+	2	$Ba(NO_3)_2$	ia,	2	baO	+	5	ΨO <sub>2</sub>	÷	2 N <sub>2</sub>	-5078
10	La	+	6	$Li(NO_3)$	=	3	Li <sub>2</sub> 0	+	5	La 203	+	3 N <sub>2</sub>	-5067
3	Be	+	2	$\Lambda g (NO_2)$	=		Ag <sub>2</sub> O	+	3	BeO	+	N <sub>2</sub>	-5064
10	Sc	+		ri (NO3)	===	3	L1 20	+	5	Sc 203	+	3 N <sub>2</sub>	-5062
5	H£	+		Ba(NO <sub>3</sub> ) <sub>2</sub>	==	2	BaO	+	5	Hf03	+	2 N <sub>2</sub>	-5034
10	Pr	+	6	Li(NO <sub>3</sub> )	=	3	Li <sub>2</sub> 0	+	5	Pr <sub>2</sub> 0 <sub>3</sub>	+	3 N <sub>2</sub>	-5012
10	Al	+	6	Na (NO <sub>3</sub> )	<del>=</del>	3	$Na_2O$	÷	5	Al 203	÷	3 N <sub>2</sub>	-4991
10	€e	+		ri(NO3)	<b>23</b>	3	Li <sub>2</sub> 0	<del>.</del> -	5	Ce <sub>2</sub> 0 <sub>3</sub>	+	3 N <sub>2</sub>	-4988
5	Mg	÷		Li (NO <sub>3</sub> )	=		Ligo	÷		MgO	+	м <sup>5</sup>	-4936
10	Ti	+	6	$Ag(NO_3)$	=	3	ya 50	÷	5	Ti 203	+	3 N <sub>2</sub>	-4932
				Ba (NO <sub>3</sub> ) 2					5	Al 203	+	3 N <sub>2</sub>	-4927
				$Sr(NO_3)_2$								3 N <sub>2</sub>	
				rī (no³)								-	
				bp(NO3) 5								ę.	
				Pb(NO3) 2									
				$Ag(NO_3)$		3	Ag <sub>2</sub> O	+	5	B <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-4842
5	Be	+	2	к (ио <sup>3</sup> )	<b>3</b>		к <sub>2</sub> 0	+	5	BeO	+	N <sub>2</sub> .	-4831

Table 12 (cont.)

				R	eac	ction						Enthalpy, cal/cc
22	Sc	+	6	$Pb(NO_3)_2 =$	3	Pb <sub>2</sub> O	+	11	Sc 203	+	6 N <sub>2</sub>	-4830
5	Ве	+	2	$Rb(NO_3) =$		Rb <sub>2</sub> O	+	5	BeO	+	$N_2^{-}$	-4821
22	Ta	+	10	$Pb(NO_3)_2 =$	5	Pb <sub>2</sub> O	+	11	Ta <sub>2</sub> O <sub>5</sub>		10 N <sub>2</sub>	-4821
22	Pr	+	6	$Pb(NO_3)_2 =$	3	Pb20	+	11	Pr <sub>2</sub> 0 <sub>3</sub>	+	6 N <sub>2</sub>	-4804
22	Ce	+	6	$Pb(NO_3)_2 =$	3	Pb <sub>2</sub> O	+	11	Ce <sub>2</sub> O <sub>3</sub>	+	6 N <sub>2</sub>	-4777
10	В	+	3	$Sr(NO_3)_2 =$	5	SrO	+	5	B <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-4775
5	Th	+	4	$Na(NO_3) =$	2	Na <sub>2</sub> O	+	5	ThO <sub>2</sub>	4.	2 N <sub>2</sub>	-4774
10	Nd	+	3	$Ca(NO_3)_2 =$	3	CaO	+	5	$Nd_2O_3$	+	3 N <sub>2</sub>	-4773
10	La	+	3	$Ca(NO_3)_2 =$	3	CaO			La <sub>2</sub> O <sub>3</sub>			-4772
10	٤c	+	3	$C_{8}(NO_{3})_{2} =$	3	CaO	+	5	Sc 203	+	3 N <sub>2</sub>	-4733
11	Mg	+	2	$Pb(NO_3)_2 =$		Pb <sub>2</sub> O	+	11	MgO	+	2 N <sub>2</sub>	-4729
5	Th	+	2	$Ba(NO_3)_2 =$	2	BaO	+	5	ThO2	+	2 N <sub>2</sub>	-4728
10	Pr	+	3	$Ca(NO_3)_2 =$	3	CaO	+	5	Pr <sub>2</sub> 0 <sub>3</sub>	+	3 N <sub>2</sub>	-4716
5	Zr	+	1	$Na(N)_3 =$		Na <sub>2</sub> O	+	5	ZrO2	⊀•	2 N <sub>2</sub>	-4708
2	ИÞ	÷	2	$Li(NO_3) =$		Li <sub>2</sub> 0	+		Nb205	+	N <sub>2</sub>	-4707
10	Ce	+	3	$Ca(NO_3)_2 =$	3	CaO	+	5	Ce <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-4688
2	Ta	+		$Ca(NO_3)_2 =$		CaO	+		Ta205	+	N <sub>2</sub>	-4683
3	Вe	+	2	$Na(NO_2) =$		Na <sub>2</sub> O	+	3	BeO	+	N <sub>2</sub>	-4670
5	Zr	+	2	$Ba(NO_3)_2 =$	2	BaO	+	5	$zr_{2}$	+	2 N <sub>2</sub>	-4658
5	Mg	+		$Ca(NO_3)_2 =$		CaO	+	5	MgO	+	N <sub>2</sub>	-4641
10	La	+	6	$Ag(NO_3) =$	3	Ag <sub>2</sub> O	+	5	La <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-4640
3	Be	+		$Ba(NO_2)_2 =$		BaO	+	3	BeO	+	* 2	-4640
10	La	+	3	$Sr(NO_3)_2 =$	3	SrO	+	5	La <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-4591
10	Sc	+			3	Ag <sub>2</sub> 0	+	5	sc203	+	3 N <sub>2</sub>	-4589
				$Pb(NO_3)_2 =$		_			-		•	-4587
				$Sr(NO_3)_2 =$				5	ид <sub>2</sub> 03	+	3 N <sub>2</sub>	-4584
10	Pr	+	6	$Ag(NO_3) =$	3	Ag <sub>2</sub> O	+	5	Pr <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-4584
10	V	+	6	$Li(NO_3) =$	3	Li <sub>2</sub> 0	+	5	$v_2o_3$	4	3 N <sub>2</sub>	-4571
10	Ce	+	6	$Ag(NO_3) =$	3	Ag <sub>2</sub> 0	+	5	Ce <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-4556
10	Pr	+	3	$Sr(NO_3)_2 =$	3	SrO	+	5	Pr <sub>2</sub> O <sub>3</sub>	4	3 N <sub>2</sub>	-4531

Table 12 (cont.)

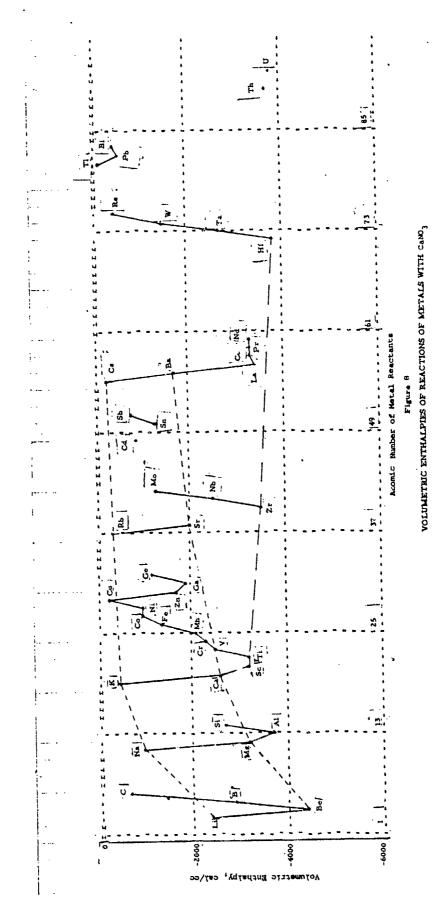
					R	eaction							Enthalpy,
10	Sc	+	3	$Sr(NO_3)_2 =$	3	Sr0	+	5	Sc.,03	+	3	N <sub>2</sub>	-4531
5	Mg	+		$Ag(NO_3) =$		Ag <sub>2</sub> 0	+	5	MgO	+		N <sub>2</sub>	-4512
10	Се	+		$Sr(NO_3)_2 =$	3	Sr0	+	5	Ce <sub>2</sub> O <sub>3</sub>	+	3	N <sub>2</sub>	-4501
2	$\mathtt{Ta}$	+	2	$Ag(NO_3) =$		Ag <sub>2</sub> O	+		Ta <sub>2</sub> O <sub>5</sub>	+		N 2	-4489
5	Si	+		$Ca(NO_3)_2 =$	2	CaO	+	5	SiO <sub>2</sub>	+	2	N <sub>2</sub>	-4467
5	Mg	+		$sr(NO_3)_2 =$		3r0	+	5	MgO	+		N <sub>2</sub>	-4454
3	U	+		$Ag(NO_2) =$		Ag <sub>2</sub> O	+	3	υ0 <sub>2</sub>	÷	2	$N_2$	-4433
10	Υì	+	6	$Na(NO_3) =$	3	Na <sub>2</sub> O	+		Ti <sub>2</sub> 0 <sub>3</sub>	+	3	N <sub>2</sub>	-4409
22	МÞ	+		$Pb(NO_3)_2 =$		Pb20	+		Nb <sub>2</sub> 0 <sub>5</sub>			N <sub>2</sub>	-4408
3	HF	+	4	$Ag(NO_2) =$	2	Ag <sub>2</sub> O	+	3	HfO <sub>2</sub>	+	2	N 2	-4407
10	Cr	+	6	$ri(NO_3) =$		, <sub>2</sub> 0	+	5	$\operatorname{Cr}_2 \overline{\operatorname{O}}_3$	+	3	$N_2$	-4405
2	Ta	+		$SE(NO_3)_2 =$		Sr0	+		Ta 205			$N_2$	-4399
5	Ве	+		$Cs(NO_3) =$		Cs <sub>2</sub> 0	+	5	ВеО	+		$N_2$	<b>-4377</b>
10	Ti	+	3	$Ba(NO_3)_2 =$	3	BaO	+	5	Ti <sub>2</sub> 0 <sub>3</sub>	+	3	$N_2$	-4373
2	Al	+	2	$Ag(NO_2) =$		Ag <sub>2</sub> O	+		Al <sub>2</sub> 0 <sub>3</sub>			N <sub>2</sub>	-4323
22	V	+	6	$Pb(NO_3)_2 =$	3	Pb20	+	11	v <sub>2</sub> o <sub>3</sub>	+	6	$^{\rm N}_2$	-4306
5	Si	+	4	$Ag(NO_3) =$	2	Ag <sub>2</sub> O	+	5	SiO <sub>2</sub>	+	2	N <sub>2</sub>	-4303
2	Nb	+		$Ca(NO_3)_2 =$		CaO	+		Nb <sub>2</sub> 0 <sub>3</sub>			N <sub>2</sub>	-4 285
10	La	+		$Na(NO_3) =$		$Na_2O$	+		La <sub>2</sub> 0 <sub>3</sub>		3	N <sup>2</sup>	-4250
3	Th	+	4	$Ag(NO_2) =$	2	Ag <sub>2</sub> O	+	3	ThO <sub>2</sub>	+	2	N <sub>2</sub>	-4232
10	Nd	+	6	$Na(NO_3) =$	3	$Na_2^O$	+	5	Nd 203	+	3	N <sub>2</sub>	-4230
10	La	+	3	$Ba(NO_3)_2 =$	3	BaO	+		I.a 203			$N_2$	-4229
10	Nd	÷	3		3	BaO	+	5	Nd 203	+		_	-4 209
				$Sr(NO_3)_2 =$					SiO <sub>2</sub>				-4 207
				$Na(NO_3) =$									
10	V	+	3	$Ca(NO_3)_2 =$	3	CaO	+	5	v <sub>2</sub> 0 <sub>3</sub>	+	3	N <sub>2</sub>	-4195
10	Pr	+	દ	$Na(NO_3) =$	3	$Na_2^O$	+	5	Pr <sub>2</sub> 0 <sub>4</sub>	+	3	N 2	-4185
				$Ba(NO_3)_2 =$									
10	Pr	+	3	$Ba(NO_3)_2 =$	3	BaO	+	5	Pr <sub>2</sub> 0 <sub>3</sub>	+	3	N <sub>2</sub>	-4166
10	Sc	+	6	$Na(NO_3) =$	3	Na 20			Sc 203				

Table 12 (cont.)

				Re	eact	_ic	n	······						Enthalpy, cal/cc
10	Се	+	6	Na(NO <sub>3</sub> )	=	3	Na <sub>2</sub> O	+		5	Ce <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-4149
22	Cr	+	6	$Pb(NO_3)_2$	=	3	Pb <sub>2</sub> O	+			Cr <sub>2</sub> O <sub>3</sub>		6 N <sub>2</sub>	-4143
10	Sc			$Ba(NO_3)_2$		3	BaO	+			Sc 203		3 N <sub>2</sub>	-4143
10	Се	+		$Ba(NO_3)_2$		3	BaO	+		5	Ce <sub>2</sub> O <sub>3</sub>	+	$3 \text{ N}_2^-$	-4131
3	Zr	+	4	Ag(NO <sub>2</sub> )	==	2	Ag <sub>2</sub> 0	+			ZrO <sub>2</sub>	+	2 N <sub>2</sub>	-4126
2	Иb	+	2	$Ag(NO_3)$	=		Ag <sub>2</sub> 0	+			$Nb_2O_3$	+	N <sub>2</sub>	-4124
5	υ	+	4	K (NO3)	=	2	к <sub>2</sub> 0	+		5	vo <sub>2</sub>	+	2 N <sub>2</sub>	-4118
5	Mg	+	2	$Na(NO_3)$	==		Na <sub>2</sub> O	+		5	MgO	+	$^{\rm N}_2$	-4104
5	ŭ	+	4	$Rb(NO_3)$	=	2	Rb <sub>2</sub> C	+		5	vo <sub>2</sub>	+	2 N <sub>2</sub>	-4103
5	Нf	+	4	K(NO3)	=	2	к <sub>2</sub> 0	+		۲,	HfO <sub>2</sub>	+	2 N <sub>2</sub>	-4092
5	Mg	+		Ba(NO <sub>3</sub> ) <sub>2</sub>	=		BaO	+		5	MgO	+	N <sub>2</sub>	-4088
5	Hf	+	4	Rb(NO <sub>3</sub> )	=	2	Rb <sub>2</sub> O	+		5	$HfO_2$	+	2 N <sub>2</sub>	-4077
10	V	+	6	$Ag(NO_3)$	ĸ	3	Ag <sub>2</sub> 0	+		5	v <sub>2</sub> 0 <sub>3</sub>	+	3 N <sub>2</sub>	-4051
3	U	+	2	Ba(NO <sub>2</sub> ) <sub>2</sub>	=	2	BaO	+		3	υ0 <sub>2</sub>	+	2 N <sub>2</sub>	-4043
10	Cr	+	3	$Ca(NO_3)_2$	=	3	CaO	+		5	Cr <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-4031
3	Hf	+	2	Ba(NO2)2	=	2	BaO	+			HfO <sub>2</sub>	+	2 N <sub>2</sub>	-4022
3	U	+	4	$Na(NO_2)$	=	2	$Na_2^O$	+		3	υ0 <sub>2</sub>	+	2 N <sub>2</sub>	-4018
2	Иb	+		$Sr(NO_3)_2$	=		Sr0	+			$Nb_2O_5$	+	N <sub>2</sub>	-4006
3	Hf	+	4	Na(NO <sub>2</sub> )	=	2	$Na_2O$	+	•	3	$HfO_2$	+	2 N <sub>2</sub>	-3996
10	Al	+	6	к (ио <sup>3</sup> )	=	3	к <sub>2</sub> 0	+		5	Al <sub>2</sub> O <sub>3</sub>	+	3 N <sub>2</sub>	-3995
10	Al	+	6	$Rb(NO_3)$	==	3	Rb <sub>2</sub> O	+		5	Al 203	+	3 N <sub>2</sub>	-3980
2	Al	+		$Ba(NO_2)_2$	=		BaO	+			Al 203	+	·N2	-3940
10	V	+	3	Sr(NO <sub>3</sub> ) <sub>2</sub>	=	3	SrO	+		5	v <sub>2</sub> 0 <sub>3</sub>	+	3 N <sub>2</sub>	-3936
5	Th	+		K(NO3)		2	к <sub>2</sub> 0	+					2 N <sub>2</sub>	-3933
5	Th	+	4	$Rb(NO_3)$	=	2	$Rb_2O$	+		5	ThO <sub>2</sub>	+	2 N <sub>2</sub>	-39 20
				$Na(NO_2)$			$Na_2O$	+			Al 203	+	N <sub>2</sub>	-3906
				Ag(NO <sub>2</sub> )	=		$\text{Ag}_2\text{O}$	+					N <sub>2</sub>	-3905
				$Ag(NO_3)$	=	3	Ag <sub>2</sub> 0	+					3 N <sub>2</sub>	<del>-</del> 3895
3	Th	+	2	Ba(NO <sub>2</sub> ) <sub>2</sub>	=	2	BaO	+					2 N <sub>2</sub>	-3892
				Ag(NO <sub>2</sub> )							La <sub>2</sub> O <sub>3</sub>	+	N <sub>2</sub>	-3885

Table 12 (cont.)

				Re	eac	<u>tic</u>	on						**************************************	Enthalpy, cal/cc
2	Ta	+	2	Na(NO <sub>3</sub> )	=		Na <sub>2</sub> O	+	•		Ta <sub>2</sub> O <sub>5</sub>	+	N <sub>2</sub>	-3873
5	Mn	+	2	Li(NO <sub>3</sub> )	=		Li <sub>2</sub> 0	+	•		MnO	+	N <sub>2</sub>	<b>-</b> 3869
2	Ta	+		Ba(NO <sub>3</sub> ) <sub>2</sub>	=		BaO	+	-		Ta <sub>2</sub> O <sub>5</sub>	+	N <sub>2</sub>	-3866
3	Th	+		Na(NO <sub>2</sub> )	=	2	Na <sub>2</sub> O	+	-	3	ThO <sub>2</sub>	+	2 N <sub>2</sub>	-3859
2	Nd	+	2	$Ag(NO_2)$	=		Ag <sub>2</sub> 0	+			$Nd_2O_3$	+	N <sub>2</sub>	-3853
2	Pr	+	2	$Ag(NO_2)$	=		Ag <sub>2</sub> O	+	•		Pr <sub>2</sub> O <sub>3</sub>		N <sub>2</sub>	-3823
2	Се	+	2	$Ag(NO_2)$	=		Ag <sub>2</sub> O	+	•		Ce <sub>2</sub> O <sub>3</sub>		N <sub>2</sub>	<b>-</b> 3793
2	Sc	+	2	$Ag(NO_2)$	=		Ag <sub>2</sub> O	+	•		Sc <sub>2</sub> O <sub>3</sub>		N <sub>2</sub>	-3778
5	Zr	+	4	к (ио <sup>3</sup> )	=	2	к20	+	•		Zro <sub>2</sub>		2 N <sub>2</sub>	-3774
10	Cr	+	3	Sr(NO <sub>3</sub> ) <sub>2</sub>	=	3	SrO	+	•	5	Cr <sub>2</sub> 0 <sub>3</sub>	+	3 N <sub>2</sub>	<b>-</b> 3763
3	Mg	+		Ag(NO <sub>2</sub> )	=		Ag <sub>2</sub> 0	+	•		MgO	+	N <sub>2</sub>	-3760
5	Zr	+	4	$Rb(NO_3)$	=	2	Rb <sub>2</sub> O	+	•	5	$2r_{2}$	+	2 N <sub>2</sub>	<b>-</b> 3757
3	Zr	+	2	Ba(NO <sub>2</sub> ) <sub>2</sub>	=	2	BaO	+	-		ZrO2	+	2 N <sub>2</sub>	-3752
5	บ	+	4	Cs(NO3)	=	2	Cs <sub>2</sub> O	4	•	5	υ0 <sub>2</sub>	+	2 N <sub>2</sub>	<b>-</b> 3739
5	Si	+	4	$Na(NO_3)$	=	2	Na <sub>2</sub> O	+			sio <sub>2</sub>	+	2 N 2	-3731
5	Si	+	2	Ba (NO <sub>3</sub> ) <sub>2</sub>	=	2	BaO	+	•		SiO <sub>2</sub>	÷	2 N <sub>2</sub>	-3728
5	Нf	+		C (NO3)	=	2	Cs <sub>2</sub> O	+	•	5	Hf02	+	2 N <sub>2</sub>	-3720
3	Zr	+	4	Na(NO <sub>2</sub> )	=	2	Na <sub>2</sub> O	4	•		ZrO <sub>2</sub>	+	2 N <sub>2</sub>	-3702
11	Mn	+	2	Pb(NO <sub>3</sub> ) <sub>2</sub>	=		Pb <sub>2</sub> O	4	•	11	MnO	+	2 N <sub>2</sub>	-3686
2	В	+	2	Ag(NO <sub>2</sub> )	=		Ag <sub>2</sub> 0	4	•		B <sub>2</sub> O <sub>3</sub>	+	N <sub>2</sub>	-3681
10	Al	+	6	Cs(NO3)	=		Cs <sub>2</sub> O	+	•		A1 <sub>2</sub> 0 <sub>3</sub>	+	3 N <sub>2</sub>	-3629
5	Th	÷		Cs(NO3)	=		Cs <sub>2</sub> 0	+	•		ThO <sub>2</sub>	+	2 N <sub>2</sub>	-3615
5	Mn	+		$Ca(NO_3)_2$	=		CaO	+	•		MnO	+	_	-3602
2	La	+		$Ba(NO_2)_2$	=		BaO						N <sub>2</sub>	-3592
10	La	+	6	K(NO3)	==	3	к20	+						-3588
5	Ca	+	2	$Li(NO_3)$	=		Li <sub>2</sub> 0	+		5	CaO	+	N <sub>2</sub>	_3585
10	La	+	6	$Rb(NO_3)$	=	3	Rb 20	+	•	5	La <sub>2</sub> O <sub>2</sub>	+	3 N <sub>2</sub>	-3574
				Ba(NO <sub>2</sub> ) <sub>2</sub>							-		N <sub>2</sub>	-3557
				K(NO <sub>3</sub> )										-3548
2	La	+	2	Na(NO <sub>2</sub> )	=		Na <sub>2</sub> O	+			La <sub>2</sub> O <sub>3</sub>			-3542





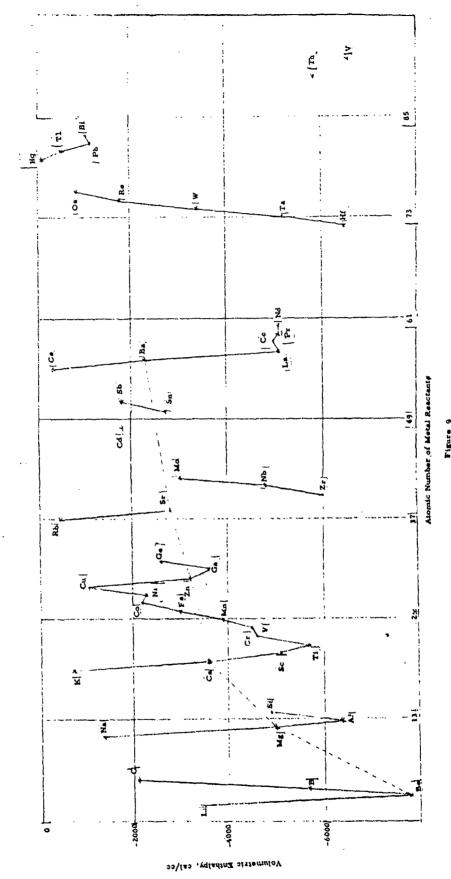


Figure 9 VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH Lino<sub>3</sub>

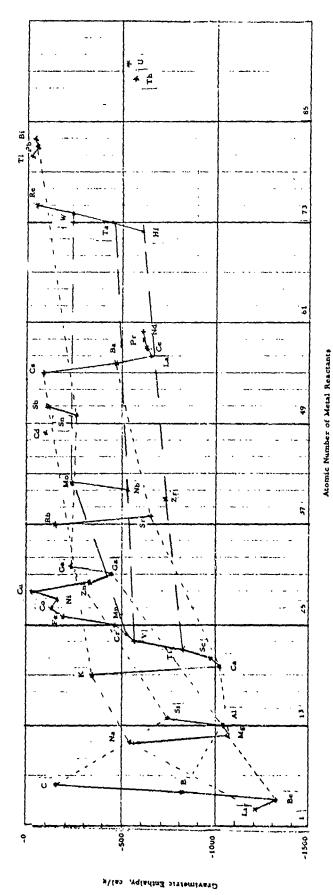


Figure 10 gravimetric enthalpies of reactions of metals with  $z_{abo}$ 

the products and reactants are the same except for boric oxide and aluminum oxide. Thus the coefficients of the reaction, the heat of formation, the volume of the nitrate, and the volume of the resultant oxide are not involved in the fact that aluminum reactions are more energetic than boron reactions. The remaining factors contributing to the reaction enthalpy are the atomic volumes of boron and aluminum and the heats of formation of boric oxide and aluminum oxide. Since boron's atomic volume. 4.57 cc. is much less than that of aluminum, 9.99 cc. its reactions would be expected to be more energetic. However, the unusually high heat of formation of aluminum oxide compared with that of boric oxide. -399 and -302 kcal, respectively, causes the aluminum reactions to be especially energetic. The effect of the heat of formation is enhanced by the stoichiometric coefficient of these oxides in the balanced equation because these factors multiply the difference between the heats of formation.

Comparison of beryllium and magnesium illustrates this further. Beryllium has a much lower atomic volume than magnesium, 4.94 compared with 13.95 cc. But unlike aluminum and boron, the heat of formation of magnesium oxide is slightly less than that of beryllium oxide, -144 compared with -146 kcal, so that beryllium reactions are more energetic than magnesium reactions. A similar situation in reverse exists with carbon. Its reaction energies are low compared with those of silicon because of the low heat of formation of carbon dioxide compared with that of silicon dioxide, -94 compared with -205 kcal.

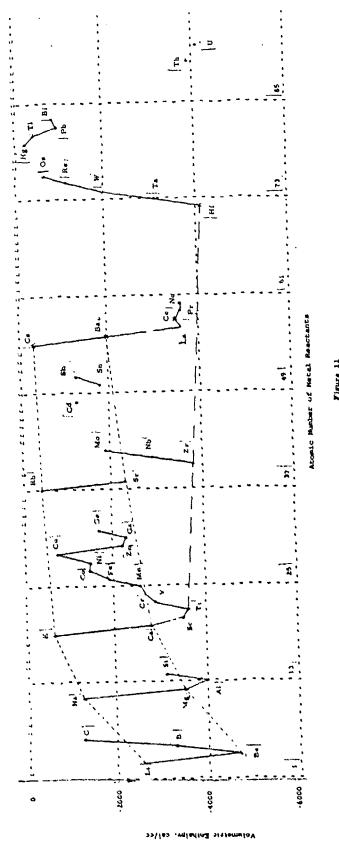
Except for these anomalies, the reactions in a group become less energetic with increasing atomic number of the metal reactant. Group I has the least energetic reactions and Group II the most energetic. Group I reactions are not energetic because of the large atomic volumes of the metals and the low heats of formation of the oxides. The Group II and VI reactions are intermediate between the Group I and II extremes.

The dashed lines in Figure 8 connect members of the "short" groups in the periodic table. These groups also have an interesting behavior. In the first three groups in the series, Group IIIB (scandium, yttrium, and lanthanum), Group IVB (titanium, zirconium, and hafnium), and Group VB (vanadium, niobium, and tantalum), the reaction energy increases with increasing atomic number. The remaining groups, Group VIB (chromium, molybdenum, and tungsten), Group VIIB (manganese, technetium, and rhenium), Group VIII (iron, ruthenium, dysprosium, cobalt, rhodium, iridium, nickel, palladium, and platinum), Group IB (copper, silver, and gold), and Group IIB (zinc, cadmium, and mercury), exhibit a decrease in energy with increasing atomic number. The members of Group VIII are not

evident because their reactions in general have a positive enthalpy and are not recorded. As drawn in Figure 8, the dashed lines (only one is drawn in for reference) connecting the members in Groups IIB, IVB, VB, VIB, VIIB, and IIB start with a negative slope for Group IIB and become more positive for each group in the above order. Some of the reasons for this behavior have been discussed previously with respect to the lanthanide contraction.

Figures 9, 10, and 11 illustrate that the reactions of metals with other nitrates or nitrites exhibit the same behavior except for vertical displacement of the ordinate scale. The two nitrates chosen represent the extremes of reaction energy with any particular metal, lithium nitrate (Figure 9) being the most energetic and cesium nitrate (Figure 10) the least energetic of those included in this study.

The gravimetric relationships are essentially the same as the volumetric ones (Figures 9 and 11 versus Figure 10) except for reversal of the magnesium and aluminum energies. Magnesium is more energetic on the gravimetric basis because the small atomic volume of aluminum is not involved. The energy decreases with increasing atomic number of the Group IIB and IVB elements. These elements behave normally on a gravimetric basis because the lanthanide contraction is not involved,



volumetric exthalpies of reactions of metals with  $\text{Ba(NO}_2)_2$ 

## D. Silicide Reactions

The reactions of various metals with 36 silicides are represented by 302 reactions in the present study. Six typical reactions are shown in Table 13, and the 50 most energetic reactions are shown in Table 14. Table 14 shows that the silicide reactions with barium metal are the most energetic. This is because BaSi3 has an unusually high heat of formation -407 kcal. When barium is the reactant, Ba2Si2 may also form and result in a less energetic reaction. Strontium also produces moderately energetic reactions, because the heats of formation of SrSi2 and SrSi are -150 and -113 kcal respectively. With the exception of these four silicides, the heats of formation of the silicides for which data are available are very low. In fact, the remainder serve preferentially as reactants because of their low heats of formation.

The periodic behavior of enthalpies of these reactions as typified by the cobalt disilicide reactions is shown in Figure 12 Because of the paucity of data, only the Group II metal reactions are available for comparative purposes. The behavior of the Group II silicides is the reverse of that exhibited by the nitrates and oxides; i.e., magnesium is least energetic and barium is most energetic. This occurs because barium silicide has a much higher heat of formation than magnesium silicide, whereas barium oxide has a lower heat of formation and a larger molecular volume than magnesium oxide

The gravimetric behavior is shown in Figure 13. It is essentially the same as the volumetric behavior. The energy of the Group II elements increases with increasing atomic number.

Although experimental studies of silicide reactions are of great interest, they would be time-consuming because very few of the reactants are available and would have to be synthesized individually.

Table 13

DATA ON REACTIONS OF VARIOUS METALS WITH SILICIDES

	Sr +	co,Si =	= 2 Co	+ SrSi
Heat of formation Molecular Weight Density Melting point, "C Boiling point, "C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	87.63 2.60 770.00 1384.00 -85.40 4.35 -365,63	-27.60 145.94 7.28 1325.00	58.94 8.90 1493.00 3100.00	-113.00
	Sr +	CoSi	= Co	+ SrSi
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	87.63 2.60 770.00 1384.00 -89.00 3.68 -509.65	-24.00 87.00 6.30 1390.00	58.94 8.90 1493.00 3100.00	-113.00
	2 Sr +	CoSi.2	GO =	+ 2 SrSi
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	87.63 2.60 770.00 1384.00 -201.40 3.26 -693.72 -2259.95	-24.60 115.06 5.30 1275.00	58.94 8.90 1493.00 3100.00	-113.00

Table 13 (cont.)

	2 Ba +	3 CoSi	II 2	3 Co	+ 2 BaSi <sub>3</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	137.36 3.50 704.00 1638.00 -740.20 4.32 -1194.06 -5153.89	-24.60 115.06 5.30 1275.00	0900	58,94 8,90 1493.00 3100,00	<u>-407.00</u> 221.63
	Ba	+ CoSi	3 =	တ	+ BaSi <sub>3</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	137.36 3.50 704.00 1638.00 -381.40	_25.60 143.21 1305.00	60 21 00	58.94 8.90 1493.00 3100.00	-407.00
	Ba	+ 3 Fesi	<b>!</b>	3 Fe	+ BaSi <sub>3</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	137.36 3.50 704.00 1638.00 -349.40 -897.99 -4339.68	-19.8 83.9 6.3 1430.0	20 91 10 00	55,85 7,86 1535,00 2800,00	_407.00

Table 14

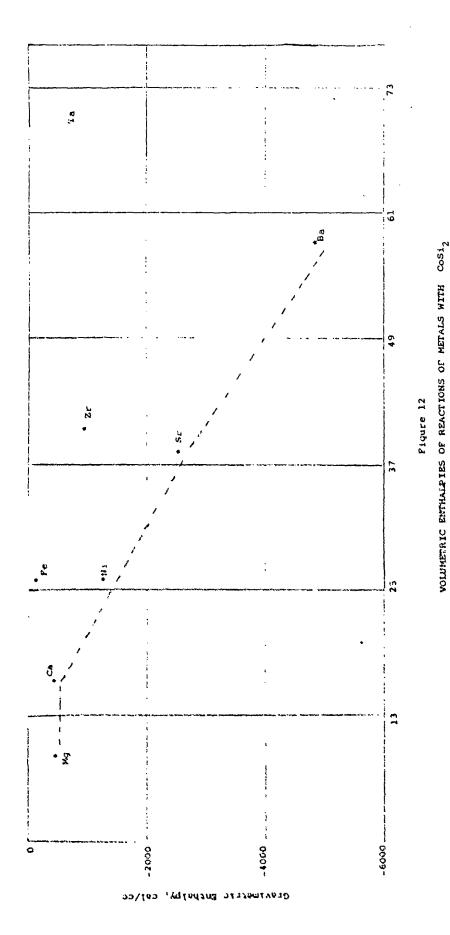
MOST ENERGETIC SILICIDE REACTIONS\* WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

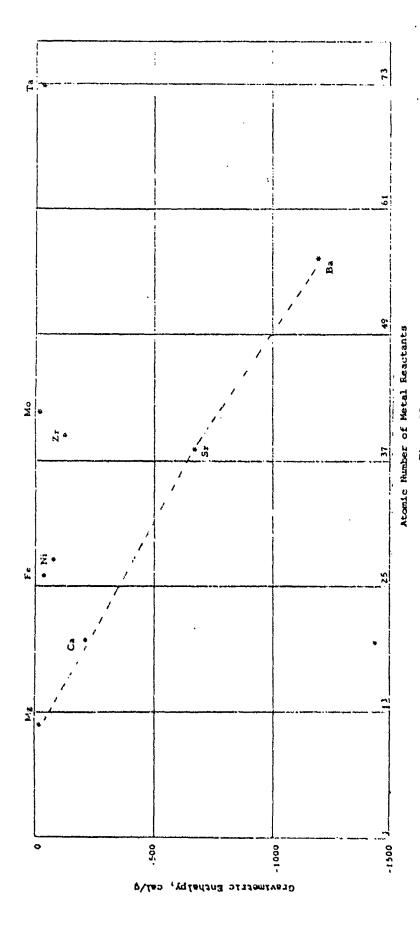
	,	
Reactant	Product	Enthalpy, cal/cc
3 CoSi <sub>2</sub>	2 BaSi <sub>3</sub>	-5153
3 FeSi	BaSi <sub>3</sub>	-4339
3 ZrSi <sub>2</sub>	2 BaSi3	-4174
3 CoSi	BaSi3	-4152
3 CaSi <sub>2</sub>	2 BaSi <sub>3</sub>	<b>-</b> 3639
CoSi <sub>2</sub>	Ba <sub>2</sub> Si <sub>2</sub>	-3417
3 Co <sub>2</sub> si	BaSi <sub>3</sub>	-3262
2 FeSi	Ba <sub>2</sub> Si <sub>2</sub>	<b>-</b> 3099
3 Ni <sub>2</sub> Si	BaSi <sub>3</sub>	-3065
zrsi <sub>2</sub>	Ba <sub>2</sub> Si <sub>2</sub>	-3045
2 CoSi	Ba <sub>2</sub> Si <sub>2</sub>	-3006
CaSi <sub>2</sub>	Ba <sub>2</sub> Si <sub>2</sub>	- 28 29
2 Cu <sub>2</sub> Si	Ba <sub>2</sub> Si <sub>2</sub>	<b>-</b> 26 29
2 Ni <sub>2</sub> Si	Ba <sub>2</sub> Si <sub>2</sub>	- 25 21
CoSi <sub>2</sub>	SrSi <sub>2</sub>	-2263
CoSi <sub>2</sub>	2 SrSi	-2259
FeSi	SrSi	-1976
ZrSi <sub>2</sub>	2 SrSi	-1946
CoSi	SrSi	-1873
2 FeSi	SrSi <sub>2</sub>	-1823
CaSi <sub>2</sub>	1 Orsi	-1793
ZrSi <sub>2</sub>	SrSi <sub>2</sub>	-1783
2 CoSi	SrSi 2	-1663
Co <sub>2</sub> Si	SrSı	-1588
CaSi 2	SrSi <sub>2</sub>	-1578
Ni <sub>2</sub> Si	SrSi	-1472

Table 14 (cont.)

Reactant	Product	Enthalpy, cal/cc
2 Co <sub>2</sub> Si	SrSi <sub>2</sub>	-1284
~	<del></del>	-1117
2 Ni <sub>2</sub> Si	SrSi <sub>2</sub>	
3 CoSi <sub>2</sub>	2 Zr <sub>5</sub> Si <sub>3</sub>	-1055
CoSi <sub>2</sub>	2 Zr <sub>2</sub> Si	- 957
CoSi <sub>2</sub>	2 ZrSi	- 916
CoSi <sub>2</sub>	2 Ni <sub>2</sub> Si	<b>-</b> 885
3 FeSi	zr <sub>5</sub> si <sub>3</sub>	<b>- 7</b> 89
CoSi <sub>2</sub>	2 Ni <sub>3</sub> Si	<b>-</b> 757
FeSi	Zr <sub>2</sub> Si	~ 728
3 CaSi <sub>2</sub>	2 Zr <sub>5</sub> Si <sub>3</sub>	- 716
CaSi <sub>2</sub>	2 Zr <sub>2</sub> Si	- 670
3 CoSi	zr <sub>5</sub> si <sub>3</sub>	- 661
CoSi <sub>2</sub>	Ca <sub>2</sub> Si <sub>2</sub>	- 645
CoSi <sub>2</sub>	2 CaSi	- 645
CoSi	Zr <sub>2</sub> Si	- 614
CoSi <sub>2</sub>	2 Ca <sub>2</sub> Si	- 602
FeSi	ZrSi	- 574
ZrSi <sub>2</sub>	2 Ni <sub>2</sub> Si	- 551
FeSi	Ni <sub>2</sub> Si	- 534
CaSi <sub>2</sub>	2 ZrSi	- 516
ZrSi <sub>2</sub>	2 Ni <sub>3</sub> Si	- 501
FeSi	Ni <sub>3</sub> Si	- 485 •
3 Co <sub>2</sub> Si	zr <sub>5</sub> Si <sub>3</sub>	- 484
CaSi,	2 Ni <sub>2</sub> Si	- 480
2	2 2 2	

The first reaction, for example, is:  $2 \text{ Ba} + 3 \text{ CoSi}_2 = 3 \text{ Co} + 2 \text{ BaSi}_3$ .





GRAVIMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CoSI<sub>2</sub>

## E Carbide Reactions

Based on the data available for 30 carbides, 386 reactions were analyzed. The carbide reactions are not a very energetic class. The most energetic reactions are listed in Table 15. Tantalum, titanium, and zirconium are the most energetic metal reactants, forming tantalum carbide, titanium carbide, and zirconium carbide, respectively. Many different carbides, e.g., lithium carbide, vanadium carbide, tungsten carbide, calcium carbide, and trichromium dicarbide, perform as useful reactants. Three representative reactions are shown in Table 16.

The reactions of a few of the metals with lithium carbide are shown in Figure 14. Although no useful correlations can be made because of the lack of data, Figure 14 does show that tantalum, titanium, and zirconium are the most energetic metals in these systems.

Table 15

MOST ENERGETIC CARBIDE REACTIONS\* WITH METALS,

IN TERMS OF VOLUMETRIC ENTHALPY

<u>Reactant</u>	<u> Product</u>	Enthalpy,
Li <sub>2</sub> C <sub>2</sub>	2 TaC	-2532
vc	TaC	-2351
WC	TaC	-2334
CaC <sub>2</sub>	2 TaC	-2222
cr <sub>3</sub> c <sub>2</sub>	2 TaC	-2186
Ni <sub>3</sub> C	TaC	-2165
Li <sub>2</sub> C <sub>2</sub>	2 TiC	-2119
Mo2C	TaC	-2056
Na <sub>2</sub> C <sub>2</sub>	2 TaC	-1987
FegC	TaC	-1956
พด	TiC	-1937
VC	Tic	-1925
UC <sub>2</sub>	2 TaC	-1900
Ni <sub>3</sub> c	TiC	-1896
cac <sub>2</sub>	2 TiC	-1853
$\operatorname{cr}_3\overline{\operatorname{c}}_2$	2 TiC	-1803
Mo <sub>2</sub> C	TiC	-1774
Mn <sub>3</sub> C	TaC	-1717 ,
Al <sub>4</sub> C <sub>3</sub>	3 TaC	-1713
Na <sub>2</sub> C <sub>2</sub>	2. TiC	-1705
Fe <sub>3</sub> C	TiC	-1690
ThC	? TaC	-1639
sic	$T_{\mathbf{a}}C$	-1588

Table 15 (cont.)

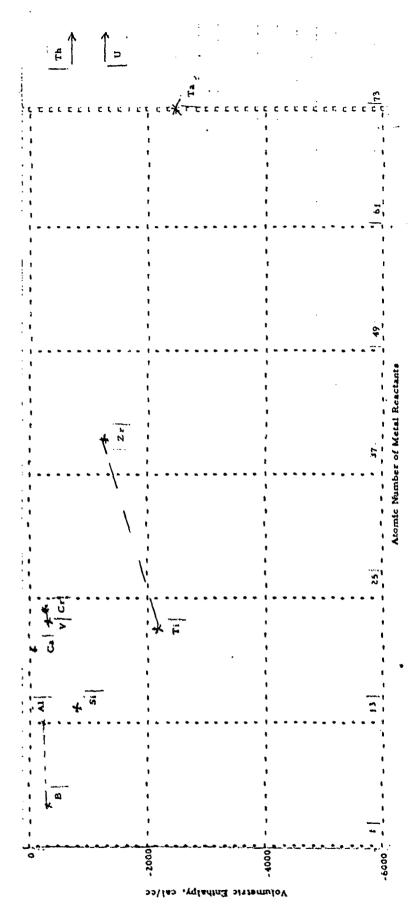
Reactant	Product	Enthalpy, _cal/cc
B <sub>4</sub> C	TaC	-1508
UC <sub>2</sub>	2 TiC	-1482
Ni <sub>3</sub> C	ZrC	-1477
Li <sub>2</sub> C <sub>2</sub>	2 ZrC	-1472
Mn <sub>3</sub> C	TiC	-1459
Al <sub>4</sub> C <sub>3</sub>	3 TiC	-1411
NigC	UC	-1402
Li <sub>2</sub> c <sub>2</sub>	2 UC	-1358
Mo <sub>2</sub> C	ZrC	-1351
WC	ZrC	-1340
CaC <sub>2</sub>	2 ZrC	-1307
Fe <sub>3</sub> Ĉ	ZrC	-1298
vc	ZrC	-1291
Na <sub>2</sub> C <sub>2</sub>	2 ZrC	-1289
Mo <sub>2</sub> C	UC	-1267
ThC <sub>2</sub>	2 TiC	-1263
cr <sub>3</sub> c <sub>2</sub>	2 ZrC	-1244
ИрС	TaC	-1237
WC	UC	-1223
B <sub>4</sub> C	TiC	-1220
Fe <sub>3</sub> C	UC	-1216
Na <sub>2</sub> C <sub>2</sub>	2 UC	-1202
CaC <sub>2</sub>	2 UC	-1196
SiC	TiC	-1181
VC	UC	-1163
Cr <sub>3</sub> C <sub>2</sub>	2 UC	-1125
Mn <sub>3</sub> C	ZrC	-1102

The first reaction, for example, is: 2 Ta + Li<sub>2</sub>C<sub>2</sub> = 2 Li + 2 TaC.

Table 16

DATA ON REACTIONS OF VARIOUS METALS WITH CARBIDES

	2 Ta	+	Li <sub>2</sub> C <sub>2</sub>	u	2 Li	+	2 TaC
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/c	180.95 16.60 2977.00 4100.00 -113.40 -283.64 -2532.90		-14.20 37.90 1.65		6,94 0,53 180,00 1326,00		-63.80 192.87 14.65 3827.00 5500.00
	3 Та	+	$^{\mathrm{Mg}_2^{\mathrm{C}_3}}$	u	2 Mg	+	3 TaC
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of restion, kcal Reactants' Gensity Gravimetric enthalpy, cal/g	180.95 16.60 2977.00 4100.00 -210.40		19.00		24.32 1.74 650.00 1120.00		-63.80 192.87 14.65 3827.00 5500.00
	2 Ta	+	$MgC_2$	11	Mg	+	2 TaC
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	180.95 16.60 2977.00 4100.00 -148.60		21.00		24,32 1,74 650,00 1120,00		-63,80 192.87 14,65 3827.00 5500.00



Lumetric enthalpies of reactions of metals with  $\mathtt{Lic}_2$ 

## F. Sulfide Reactions

The data for 68 sulfides were used to calculate the enthalpies of 2145 reactions of sulfides with metals. These reactions are, in general, only moderately energetic. The 50 most energetic reactions are shown in Table 17. The reactions of iron disulfide with thorium, cesium, and lanthanum are the most energetic. The energies of these reactions are not considered high for pyrotechnic materials but are high enough to warrant a modest experimental study. In most cases several sulfide products, involving different valences of the metals, form from the same two reactants. It would be interesting to determine which reactions predominate, since this will define the experimental reaction energy. This energy is a function of the kinetics of the reaction and the thermodynamic equilibrium based on free energies. A few representative reactions are shown in Table 18.

Figure 15 illustrates the periodic relationships between the reactions of metals with iron disulfide. The relationship is essentially the same as that among the nitrate reactions except for some differences with the low-atomic number metals. For instance, in the sulfide systems the Group II metals exhibit a maximum energy output at calcium, whereas in the nitrate systems beryllium and magnesium are more energetic than calcium. In the nitrate systems, the energy output based on the volume of reactants decreases in going from beryllium to barium because the product oxides all have approximately the same heats of formation, -133 to -152 kcal, and the reactant metals increase in atomic volume, 4.74 to 39.2 cc. In the sulfide systems, the effect of the reactant volumes is the same, but the heats of formation vary widely, with a pronounced maximum (-115 kcal) at calcium sulfide and a minimum (-56 kcal) at beryllium sulfide. In this case, the effect of the heats of formation predominates and the energy outputs also have a maximum at calcium. Another interesting difference between the sulfide and nitrate systems is that in the former aluminum is less energetic than magnesium and in the latter the reverse is true. This phenomenon results from the unusually high heat of formation of aluminum oxide, -399 kcal.

Table 17

NOST ENERGETIC SULFIDE REACTIONS\* WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

Product	Enthalpy, cal/cc
	-3169
· · · · · · · · · · · · · · · · · · ·	
<del>-</del> -	-3104
2 Th <sub>4</sub> S <sub>7</sub>	-3093
2 Ce <sub>2</sub> S <sub>3</sub>	-3089
2 ThS	_3074
2 La <sub>2</sub> S <sub>3</sub>	-3061
Ce₃S₄	-3038
2 Ce <sub>2</sub> S <sub>3</sub>	-3018
2 ThS	-3018
2 CeS	<b>-299</b> 5
2 La <sub>2</sub> 3 <sub>3</sub>	- 2993
2 CeS	-2939
ThS <sub>2</sub>	<b>-29</b> 35
3 Th <sub>4</sub> S <sub>7</sub>	-2920
3 ThS	-2894
3 Ce <sub>3</sub> S <sub>4</sub>	-2892
Ce <sub>2</sub> S <sub>3</sub>	-2865
ThS <sub>2</sub>	-2851
La <sub>2</sub> S <sub>3</sub>	-2849
3 CeS	-2822 .
4 ThS	-2781
4 Th <sub>4</sub> S <sub>7</sub>	-2769
Ce <sub>3</sub> S <sub>4</sub>	-2760
4 Ce <sub>2</sub> S <sub>3</sub>	-2726
4 La <sub>2</sub> S <sub>3</sub>	-2715
4 CeS	-2711
	2 Ths  2 La 2 <sup>S</sup> 3     Ce 3 <sup>S</sup> 4  2 Ce 2 <sup>S</sup> 3  2 Ths  2 Ces  2 La 2 <sup>S</sup> 3  2 Ces  Ths 2  3 Th <sub>4</sub> S <sub>7</sub> 3 Ths  3 Ce 2 <sup>S</sup> 3  Ths 2  La 2 <sup>S</sup> 3  Ths 2  La 2 <sup>S</sup> 3  4 Ce 2 <sup>S</sup> 3  4 Ce 2 <sup>S</sup> 3  4 La 2 <sup>S</sup> 3

Table 17 (cont.)

	· · · · · · · · · · · · · · · · · · ·	
Reactant	Product	Enthalpy, _cal/cc
Nis	ThS	-2708
2 Co <sub>2</sub> S <sub>3</sub>	3 Ths <sub>2</sub>	-2695
4 NiS	Ce <sub>3</sub> S <sub>4</sub>	-2678
7 Nis	Th <sub>4</sub> S <sub>7</sub>	<b>-</b> 2675
CoS	Ths	-2667
Nis	CeS	-2641
3 Nis	Ce <sub>2</sub> S <sub>3</sub>	-2641
3 FeS <sub>2</sub>	2 Th <sub>2</sub> S <sub>3</sub>	<b>-2636</b>
3 Nis	La <sub>2</sub> S <sub>3</sub>	-2633
4 CoS	$Ce_3S_4$	<b>-2</b> 630
7 CoS	Th <sub>4</sub> S <sub>7</sub>	-2621
ReS <sub>2</sub>	2 Ths	-2615
CuS	Ths	-2612
CoS	CeS	-2600
ws <sub>2</sub>	2 Ths	-2599
3 CoS	Ce <sub>2</sub> S <sub>3</sub>	-2590
3 CoS	La <sub>2</sub> S <sub>3</sub>	-2584
4 CuS	$Ce_3S_4$	-2571
2 ReS <sub>2</sub>	Ce3S4	- 25 70
FeS <sub>2</sub>	CeS <sub>2</sub>	- 2568
CS <sub>2</sub>	2 ThS	-2563
3 FeS <sub>2</sub>	2 Th <sub>2</sub> S <sub>3</sub>	-2560
7 CuS	Th <sub>4</sub> S <sub>7</sub>	-2556
7 ReS <sub>2</sub>	2 Th <sub>4</sub> S <sub>7</sub>	-2553

The first reaction for example is: 8 Th + 7 FeS<sub>2</sub> = 7 Fe + 2 Th<sub>4</sub>S<sub>7</sub>.

Table 18

DATA ON REACTIONS OF VARIOUS METALS WITH SULFIDES

				•	ن ا ا
	3 Ce	+ 2 FeS <sub>2</sub>	11	2 Fe	+ 66324
'		-36.88			-421.50
Heat of Formation	140.13	119.98			548.65
MOLECULAR MELYING	6.70	4.87		•	
Density Malfing moint, °C	775.00	450.00		1535.00	7020,00
point.	2500.00				
Heat of reaction, kcal	-347.74				
s density	5.56				
Gravimetric enthalpy, cal/9	_3104.33				
				1	1
	3 Ce	+ 2 FeS <sub>2</sub>	u	2 Fe	+ Ce <sub>3</sub> S <sub>4</sub>
A DESCRIPTION OF THE PROPERTY		42			-421.50
Heat of formation	140,13	119.98		55.85	548.65
Molecular weight	6.70	Ŋ,	_	-	,
Density	775.00	1171.00	_	1535.00	2050.00
Melting point, c	2900.00			•	
Boiling Folia, Cal	-336.46				
	5.96				
Gravimetric enthalpy, cal/g	2030.02				
Volumetric enthalpy, cal/cc					
	3 Ce	+ 4 GaS	11	4 Ga	+ Ce <sub>3</sub> S <sub>4</sub>
8		-46.40	0		-421.50
Heat of formation	140.13	101.79	Φ	69.72	548.65
Note Contain States	6.70	3.8	'n	5.90	0
42 42 5 3	775.00	965.0	Ö	29.78	2050.00
Reling Form, of	2900.00			937.00	
ä	-235.90				
	4.92				
alpy	- 285.06				
iry, call	-1402-21		1		
ها ارموسید از ایسان فرود که بسیان به این استان که موسیقی که موسیقی این استان می این استان استان می این استان					

Table 18 (cont.)

anderson de la company	8 Th +	7 Fes <sub>2</sub>	= 7 Fe	+ 2 Th <sub>4</sub> S <sub>7</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	232.00 11.20 1840.00 4500.00 -1071.34 7.97 -397.59	-36.88 119.98 4.87 450.00	55.85 7.86 1535.00 2800.00	_665.00 1152.46 2027.00
Andrew Communication and the communication of the c	# 4T B	7 FeS <sub>2</sub>	= 7 Fe	+ 2 Th457
Heat of formation Molecular Weight Density Melting point, °C Foiling point, °C Heat of reaction, kcal Roactants' density Gravimetric enthalpy, cal/g	232.00 11.20 1840.00 4500.00 -1032.36 -382.94 -3093.80	-42.52 119.98 5.00 1171.00	55.85 7.86 1535.00 2800.00	-665.00 1152.46 2027.00
	4 Th	+ 7 GaS	a 7 Ga.	+ Th457
Hert of formation Molecular Weight Density Melting point, °C Boiling point, °C Heat of reaction, kcul Reactants' density Gravimetric enthalpy, cal/g	232.00 11.20 1840.00 4500.00 -340.20 6.13 -207.37	-46,40 101,79 3,86 965.00	69.72 5.90 29.78 937.00	_665.00 1152.46 2027.00

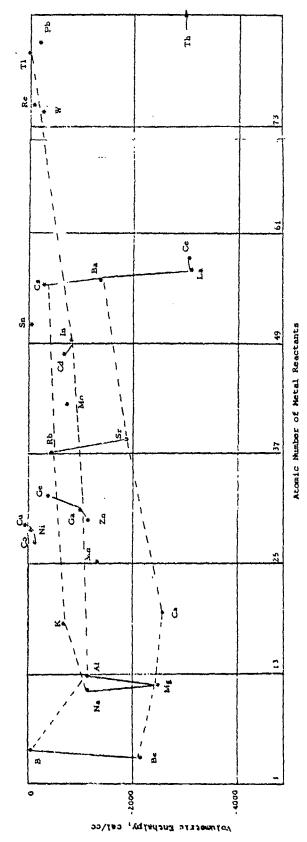


Figure 15  $^{\bullet}$  volume fric enthalpies of reactions of metals with Fes $_2$ 

## G. Nitride and Azide Reactions

The data for 44 nitrides and 13 azides were used to compute the enthalpies of 1575 reactions. These reactions, like the sulfides, are only moderately energetic and appear to warrant only a modest experimental study. Caution must be excerised in experimental work because many of the azide compounds are very reactive. The 50 most energetic reactions are listed in Table 19. The reactions of barium azide (BaN<sub>6</sub> or Ba(N<sub>3</sub>)<sub>2</sub>) with beryllium, yttrium, titanium, zirconium, hafnium, thorium, and aluminum metal are the most energetic. The reactions of iron nitride with these metals are also fairly energetic.

Several representative reactions are shown in Table 20. Certain interesting relationships are apparent. For instance, the azide or nitride of barium can be used as the reactant. The azide is more energetic because it has a lower heat of formation. Copper can also be used as a nitride or azide, but not enough data are available to calculate the volumetric enthalpies. On a gravimetric basis, the reaction of copper azide with titanium is highly energetic. In some cases more than one nitride can be used a deactant or is formed as a product from the same reactant metal. This is illustrated by the iron nitrides, Fe<sub>2</sub>N and Fe<sub>4</sub>N.

The periodic relationships of the reactions with barum azide and with the iron nitride Fe<sub>2</sub>N are shown in Figures 16 and 17. Although all the possible lines have not been drawn, it is evident that except for minor deviations the behavior of these systems closely resembles that of the oxide and nitrate systems. This is especially apparent in Groups II and III: aluminum is more energetic than magnesium.

Table 19

MOST ENERGETIC NITRIDE AND AZIDE REACTIONS\* WITH METALS,

IN TERMS OF VOLUMETRIC ENTHALPY

	·			
Re	eactant I	Pro		nthalpy, cal/cc
	BaN <sub>6</sub>	3 E	Be3N2	-3346
	•			-3308
	-	6 T		-3109
	•	6 I	rin	<b>-</b> 3087
	•	6 Z	ZrN	-3014
		6 E	HEN	-2961
2	BaN <sub>6</sub>	r 6	rh <sub>3</sub> N <sub>4</sub>	-2692
		6 A		-2499
3	Fe <sub>2</sub> N	U	<sup>J</sup> 2 <sup>N</sup> 3	-2478
2	Fe <sub>2</sub> N	E	Be <sub>3</sub> N <sub>2</sub>	-2470
	BaN <sub>6</sub>	ľ	NbN <sub>6</sub>	- 2460
	BaN <sub>6</sub>	6 7	M	-2444
	Fe <sub>2</sub> N	τ	IN	-2431
	BaN <sub>6</sub>	6 1	ran	-2423
	Fe <sub>2</sub> N	2	ZrN	-2387
	Fe <sub>2</sub> N	Ĵ	rin	-2368
	Fe <sub>2</sub> N	F	Hen	-2330
	BaN <sub>6</sub>	6 (	CeN	-2298
	BaN <sub>6</sub>	6 5	SCN	-2182
4	Fe <sub>2</sub> N	1	rh <sub>3</sub> N <sub>4</sub>	-2153
	CrN			-2098
3	CrN	ť	<sup>J</sup> 2 <sup>N</sup> 3	-2093
	GaN			-2078
3	GaN	ι	J <sub>2</sub> N <sub>3</sub>	-2070
	CrN	2	ZrN	-2059

Table 19 (cont.)

Re	eactant	Pr	oduct I	Enthalpy, cal/cc
	CrN		Be <sub>3</sub> N <sub>2</sub>	-2057
	GaN		3 2 ZrN	-2044
2		3	Sl <sub>3</sub> N <sub>4</sub>	-2037
	Gan		Be <sub>3</sub> N <sub>2</sub>	-2037
			3 Z LaN	-2012
	BN		UN	-1994
	CrN		TiN	-1978
	CrN	1	H£N	-1970
	Jan		TiN	-1969
3	BN		<sup>U</sup> 2 <sup>N</sup> 3	-1967
	Fe <sub>2</sub> N		YN	-1964
	Z GaN	;	H£N	-1963
	BN		ZrN	-1961
2	BN		Be <sub>3</sub> N <sub>2</sub>	-1922
	Fe <sub>2</sub> N		AlN	-1907
	Fe <sub>2</sub> ti		CeN	-1901
	Fe <sub>2</sub> N	;	NON	-1894
	_	6	YN	-1878
	BN		HfN	-1869
	Fe <sub>2</sub> N		TaN	-1866
	BN		Tin	. 1864
	Bal. 6	6	BN	-1795 '
4	GaN		Th <sub>3</sub> N <sub>4</sub>	-1777
	Fe <sub>2</sub> N		JCN 4	-1776
4	CrN		Th <sub>3</sub> N <sub>4</sub>	-1766

The first reaction, for example, is: 9 Be + BaN<sub>6</sub> = Ba + 3 Be<sub>3</sub>N<sub>2</sub> N<sub>ô</sub> represents the azide  $(N_3)_2$ 

Table 20

DATA ON REACTIONS OF VARIOUS METALS WITH NITRIDES AND AZIDES

هـ الله فه ره (مه نسخه خواصه مع ره معجود ولم جه يعدنين معجود والم علي هم معرضة والمعرفة والمعرفة والمعرفة والم	3 Be	+	2 AlN		2 A1	+	Be <sub>3</sub> N <sub>2</sub>
Heat of formation Molecular weight	10′6	; 1	-57,70 40.98		;		, ·
Density Melting point, °C	1,85 128300		5 5		2.70 660 00		2200,00
	2970,00				27 .		240
s density	2.74						
Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc	186, 24 _510, 60			į	2		
	3 Be	+	2 BN	ti	2 B	+ ;	Be <sub>3</sub> N <sub>2</sub>
£0.000		i	, N	<u> </u>		i I	7
10	9 01		24 .83		10.82		O,
, 1	ج د		9		40,		2200.00
Metring Point, "C Boiling point, "C	2970,00						2240.00
reactio	1.						
Reactants: density Gravimetric enthalpy, cal/g	-1922, 64						
	9 Be	+	Bang		Ba	! +	ندي ت
	and the same same same and a same as a same as	;	); (a)	ì		i i	i io
Molecular Weight			221.41				55
1	-		:				Č
	1283 00 2970 00				704.00 1638.00		2240 00 2240 00
Heat of reaction, kcal							
s density							
Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc							
er express ten e primer de la casa desse desse de la casa de la ca	* *** ** ******* ** * * * * * * * * * *	1		1	:	i t 1	

Table 20 (cont.)

	3 Be	+	2 Fe <sub>2</sub> N		4 Fe	+	Be <sub>3</sub> N <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	9.01 1.85 1283.00 2970.00 -133.90 5.14 -480.86		125.71 6.35		55,85 7,86 1535,00 2800,00		
	3 Be	+	$2 \text{ Fe}_4^{\text{N}}$	u	8 Fe	+	$Be_3N_2$
Heat of formation Molecular weight Density Melring point, °C Bolling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	9.01 1.85 1.283.00 2870.00 -1.30.60 5.78 -260.23		-2.55 237.41 6.57		55.85 7.86 1535.00 2800.00		-135.70 55.06 2200.00 2240.00
	3 Be	+	2 GaN	il	2 Ga	+	$Be_3N_2$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/c	9.01 1.85 1.283.00 2970.00 -85.70 4.62 -440.62		-25,00 83,73 6,10		69,72 5,90 29,78 937,00		-135.70 55.06 2200.00 2240.00

Table 20 (cont.)

	6 Ti	+	BaN <sub>6</sub>	u	Ba	+	6 TiN
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	47.90 4.50 1812.00 3000.00 -430.00 -845.11		-8.00 221.41 2.94		137,36 3.50 704.00 1638.00		-73.00 61.91 5.43 2927.00
	2 T1	+	Ba3N2	II	3 Ba	+	2 Tin
Heat of formation Molecular weight	47.90		-86.90 440.10		137.36		-73.00 61.91 5.43
Density Melting point, °C Boiling point, °C Heat of reaction, kcal	4.50 1812.00 3000.00 -59.10		1000.00		704.00		2927.00
Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc	-110, 28					į   	
ŧ	2 Ti	+	Be <sub>3</sub> N <sub>2</sub>	I	3 Be	+	2 Tin
Heat of formation Molecular weight	47,90		-135,70 55,06		9.01		-73.00 61.91 5.43
Density Melting point, °C Boiling point, °C Heat of reaction, kcal	4.50 1812.00 3000.00 -10.30		200°00 2240.00		1.283.00 2970.00		2927.00
Reactants density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc	~68,28		in the second se		1		

Table 20 (cont.)

	+ II	Cu <sub>3</sub> N	= 3 Cu +	+ Tin
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/g	47.90 4.50 1812,00 3000,00 -90.80	17,80 204,63	63.54 8.92 1083.00 2582.00	-73.00 61.91 5.43 2927.00
	3 Ti +	CuN <sub>3</sub> *	= Cu +	3 Tin
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	47.90 4.50 1812.00 3000.00 -279.50	60°50 105°56	63.54 8.92 1083.00 2582.00	-73.00 61.91 5.43 2927.00
	Ti +	Fe <sub>2</sub> N =	= 2 Fe +	TiN
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	47.90 4.50 1812.00 3000.00 -72.10 5.70 -415.30	125,71 6,35	55,85 7.86 1535.00 2800.00	-73.00 61.91 5.43 2927.00

Table 20 (cont.)

	2r	+	AIN	15	Al	+	ZrN
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Keactants' density Gravimetric enthalpy, cal/g	91, 22 6, 40 1852, 00 2900, 00 - 24, 50 4, 93 -185, 22 -913, 37		220 00		26 98 2.70 660.00 2327 00		-82,20 105,23 7,09 2952,00
	Zr	+	BN	11	m l	 	ZrN
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	91.22 6.40 1852.00 2900.00 -50.10 4.54 .431.71		-32.10 24 83 2.20		10 82 2.38 2040 00 2550 00		0000
AMERICAN AMERICAN AND AND AND AND AND AND AND AND AND A	6 Zr	+	BaN6		Ba	+ 1	6 ZrN
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants density Gravimetric enthalpy, cal/g	91, 22 6, 40 185,2 00 2900,00 4, 78 631, 17 3014, 96			,	137 36 3 50 704 00 1638 00	;	-82 20 105 23 7 09 2952 00

Table 20 (cont.)

to become the contract of the	+ ZZ +	Cu <sub>3</sub> N	11	3 Cu +	_	ZrN
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	91.22 6.40 1852.00 2900.00 -100.00	17.80 204.63		63,54 8,92 1083,00 2582,00	.,	-82,20 105,23 7,09 2952,00
	3 Zr +	CuN <sub>3</sub>	11	Cu	+	3 ZrN
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	91.22 6.40 1852.00 2900.00 -307.10	60.50		63,54 8,92 1083,00 2582,00	-	-82.20 105.23 7.09 2952.00
	Zr	+ Fe <sub>2</sub> N	11	2 Fe	+	ZrN
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/c	91, 22 6, 40 185, 2, 00 2900, 00 -81, 30 6, 37 -374, 78	125.71 6.35		55.85 7.86 1535.00 2800.00		-82,20 105,23 7,09 2952,00

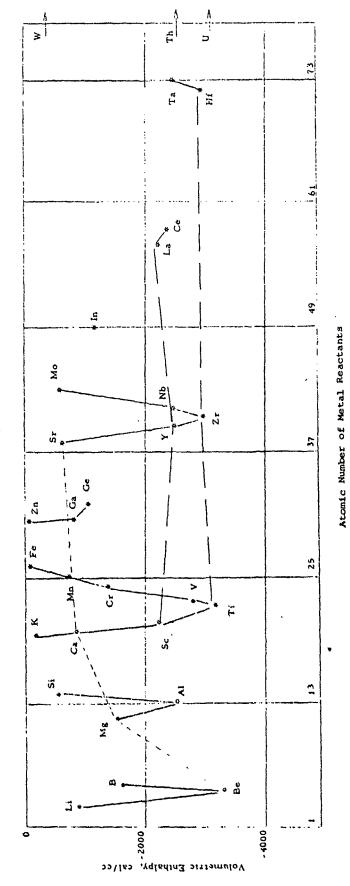
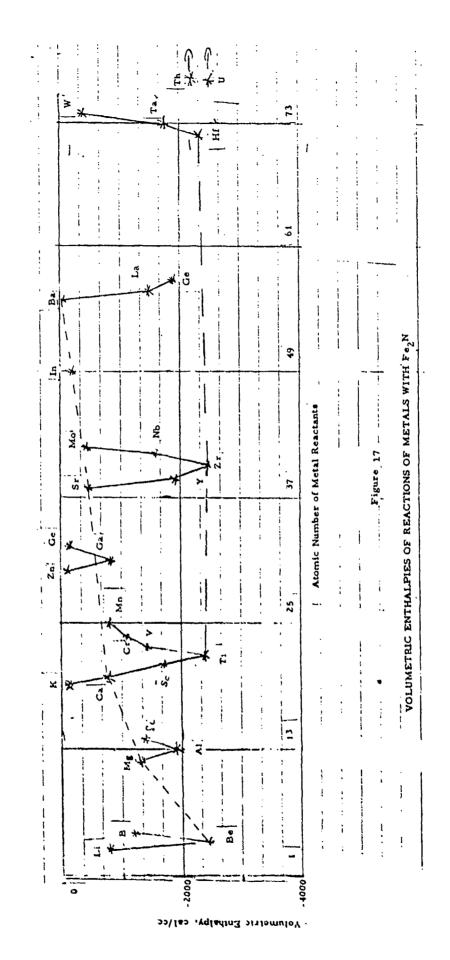


Figure 16 VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH  $Ba(N_{\rm J})_2$ 



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## H. Chlorate and Perchlorate Reactions

The possible reactions of 50 metals with 7 chlorates and 9 perchlorates resulted in the computation of 16,384 reactions. Only 801 of them were printed, because reactions with positive enthalpies were discarded, as were those with the lowest enthalpy from the possible combinations of each pair of reactants. Examples of the computer output for some of the more energetic reactions are shown in Table 21.

Chlorates and perchlorates are combinations of chlorine and oxygen systems. The chloride of the metal reactant is rarely produced, and when it is produced, it is in a very low ratio compared with its oxide. For example, note the reaction between beryllium and silver chlorate in Table 22. This occurs because the oxides of the highly reactant metals generally have higher negative heats of formation than the chlorides.

The chlorates and perchlorates are much more energetic than the comparable oxide systems. In fact, they are the most energetic systems examined. The 200 most energetic reactions are shown in Tables 22 and 23. The most energetic reaction, between beryllium and magnesium perchlorate, has a volumetric enthalpy of -9459 cal/cc, which is appreciably higher than the most energetic oxide and nitrate reactions: beryllium with ruthenium oxide, -7800 cal/cc: and beryllium with lithium nitrate, -7798 cal/cc. The beryllium-lithium perchlorate reaction, -9088 cal/cc, which is the next most energetic perchlorate reaction compares with the beryllium-lithium nitrate reaction

The chlorates and perchlorates are listed in order of their effective energies in Table 24. In general, the perchlorate of a metal is more energetic than the chlorate. Silver is an exception because the chlorate has a much higher density than the perchlorate, and thus on a volumetric basis the chlorate is more energetic than the perchlorate.

The periodic trends in the gravimetric and volumetric enthalpies are shown in Figure 18 for reactions of all the metals with magnesium perchlorate. The trends are almost the same as those in the nitrate and oxide systems. The most energetic reactions occur with beryllium, aluminum, titanium, zirconium, hafnium, and the rare earths lanthanum, cerium, praseodymium, and neodymium. The alkali metals tend to have the lowest enthalpies. These trends are essentially the same for all the oxidizers in the oxide, nitrate, and chlorate-perchlorate systems, and for the gravimetric and volumetric bases. Thus, all the curves are similar except for vertical displacement of the ordinates. This type of plot allows one to choose a metal reactant for a particular oxidizer, magnesium perchlorate in this case.

Table 21

DATA ON REACTIONS OF VARIOUS METALS WITH CHLORATES AND PERCHLORATES

- Acceptation of the amplitude to the two designs of the special party of the statement of the special party of th	1.3 Mg +	4 AgCIC3	$= 2 \text{ Ag}_2^{\text{Cl}}$	+ 12 MgO	+ MgCl <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	24.32 1.74 650.00 1120.00 -1918.36 -1773.76 -5411,93	.5.73 191.34 4.43 231.00 270.00	_30.90 251.20	143.84 40.32 3.58 2800.00	-153.40 95.23 714.00 1418.00
	13 Mn	+ 4 AgC103	= 2 Ag <sub>2</sub> CI	+ 12 MnO +	MnCl <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcai Reactants' density Gravimetric enthalpy, cal/g	54.94 7.20 1244.00 2087.00 -1258.18 5.44 -850.36	-5.73 191.34 4.43 231.00 270.00	_30.90 251.20	-92.00 70.93 5.43 1650.00	-115.30 125.84 2.98 650.00 1190.00
	Wo +	AgC10 <sub>3</sub>	= AgC1	+ MoO <sub>3</sub>	
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/g	95.95 10.20 2610.00 4800.00 -204.96 5.46 -713.43	-5.73 191.34 4.43 231.00 270.00	-30.36 143.34 5.56 455.00 1557.00	-180.33 143.95 4.50 795.00 1155.00	

Table 21 (cont.)

	13 7,n +	4 Arc10, =	2 Ag,C1 +	12 ZnO +	$\operatorname{ZnCl}_2$
formation ar weight	65.	, , ,	_30.90	-83.17 81.38 5.47	0001
c c	419.50 907.00 1136.32 5.54 -703.47	231.00		• • 1	
1	10 Zr +	6 AgClO <sub>3</sub> =	3 Ag <sub>2</sub> Cl +	. 9 ZrO <sub>2</sub> +	T 3
u	91.22	-5.73 191.34	_30.90 251.20	-258.20 123.22	-208.00 197.59
point, °C	6.40	4.43 231.00 270.00			350.00
point, °C reaction, keal	2590.1 2590.1 5.1	1			
Reactants' defibily Cal/g -1 Gravimetric enthalpy, cal/c -6 Volumetric enthalpy, cal/cc -6	1257.1 6448.1				
- 1	16 Ag +	2 AgC104 =		8 Ag 20 +	2 AgCl
u	107 87	-7.75 207.34		-7.31 231.76	-30.36 143.34
ar weight	90,0	2.81 486.00		7.14 300.00	5.56 455.00
Melting Point, oc Bolling Point, oc Heat of reaction, Kcal	2193.00 -103.67				)  - 
py, cal/g y, cal/cc	-48.43 -332.11				

Table 21 (cont.)

	2 Zr +	LICLO	= Licl	+ 2 Zro <sub>2</sub>	1
of formation cular weight ity ing point, "C ing point, "C of reaction, tants' density imetric enthal	91.22 6.40 1852.00 2900.00 -508.00 3.99 -1758.15 -7021.28	.106.10 106.50 2.43 236.00 440.00	-97 70 42.40 2.07 610.00 1382.00	258.20 123.22 5.46 2700.00 4300.00	
	8 Ag +	$Mg(\mathbf{ClO}_4)_2$	= MgO <sub>2</sub>	+ 3 Ag <sub>2</sub> 0 <sub>2</sub> +	2 AgCl
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	107.87 10.50 960.80 2193.00 -87.92 6.46 -80.95	-140.60 223.23 2.60 251.00	-148.90	-6,30 247.76 7.44 100.00	-30,36 143.34 5.56 455.00 1557.00
	16 Al + 3	$Mg(Clo_4)_2$	$= 3 \text{ MgCl}_2$	+ 8 Al 203	
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/c	26.98 2.70 660.00 2327.00 -3231.12 2.64 -2933.73 -7742.25	-140.60 223.23 2.60 251.00	-153.40 95.23 2.32 714.00 1418.00	-399.09 101.94 3.97 2015.00 3500.00	

Table 21 (cont.)

	4 Ge +	Mg (0104) 2 -	MGCI 2	$^{+}$ 4 GeO $_{2}$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	72.60 5.35 960.00 2700.00 -5.26.00 3.67 -1024.08 -3753.44	-140,60 223.23 2,60 251.00	-153.40 95.23 2.32 714.00 1418.00	-128.30 104.60 4.70 1000.00
	4 H£ +	$Mg(ClO_4)_2 =$	MgCl <sub>2</sub> <sup>F</sup>	- 4 H£O <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	178.50 13.30 2227.00 3200.00 -1098.80 6.72 -1172.39 -7874.34	50 60 00		-271.50 210.60 9.63 2810.00
	8 Hg +	$Mg(ClO_4)_2 =$	MgCl <sub>2</sub> +	8 Hg0
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	200.61 13.55 -38.87 356.57 186.24 8.95 -101.88	0 0 0 0	-153.40 95.23 2.32 714.00 1418.00	-21.68 216.61 11.14 500.00

Table 22

MOST ENERGETIC CHLORATE AND PERCHLORATE REACTIONS WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

						]	Reactio	n					Enthalpy, cal/cc
8	Ве	+		Mg(ClO <sub>4</sub> ) <sub>2</sub>	=		MgCl <sub>2</sub>	+	8	BeO			-9459
4	Ве	+		Li(ClO <sub>4</sub> )			LiCl	+	4	BeO			<b>-</b> 9088
13	Ве	+	4	Ag (C10 <sub>3</sub> )	=	2	Ag <sub>2</sub> Cl	+	12	Be0	+	BeCl <sub>2</sub>	-8103
4	U	+		$Mg(ClO_4)_2$	=		MgCl <sub>2</sub>	+	4	$\mathtt{vo}_2$		-	<b>-</b> 7989
4	Hf	+		Mg (C10 <sub>4</sub> ) <sub>2</sub>	=		MgCl <sub>2</sub>			Hf0 <sub>2</sub>			<b>-</b> 7874
3	Ве	+		Na (C103)	=		NaCl	+	3	BeO			<b>-7</b> 853
4	Ве	+		K(C104)	=		KCl	+	4	BeO			7850
16	Al	+	3	Mg (C10 <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+	8	A1203			<b>-7742</b>
2	U	+		Li(C10 <sub>4</sub> )	=		LiCl	+	2	υ0 <sub>2</sub>			<b>-</b> 7670
2	Нf	+		Li(ClO <sub>4</sub> )	=		LiCl	+	2	HfO <sub>2</sub>			<b>-</b> 7562
8	Al	+	3	Li(ClO <sub>4</sub> )	=	3	Lici	+	4	A1203			-7431
16	В	+	3	Mg(C10 <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+	8	B <sub>2</sub> O <sub>3</sub>			-7423
4	Zr	+		Mg (CLO <sub>4</sub> ) 2	=		MgCl <sub>2</sub>	+	4	ZrO2			-7318
8	Ве	+		Ba(C10 <sub>4</sub> ) <sub>2</sub>	=		BaCl <sub>2</sub>			BeO			-7302
8	В	+	3	Li(C10 <sub>4</sub> )	==	3	LiCl	+	4	B <sub>2</sub> O <sub>3</sub>			-7038
2	Zr	+		Li(ClO <sub>4</sub> )	=		LiCl	+	2	ZrO2			-7021
4	Ве	+		Rb(ClO <sub>4</sub> )	=		RbCl	+	4	BeO			-7002
4	Th	+		$Mg(ClO_4)_2$	==		MgCl <sub>2</sub>	+	4	ThO 2			-6998
10	υ	+	6	Ag(C10 <sub>3</sub> )	<b>=</b>	3	Ag <sub>2</sub> Cl	+	9	UO <sub>2</sub>	+	ucl3	-6989
16	Ti	+	3	$Mg(C10_4)_2$	=	3	MgCl <sub>2</sub>	+	8	Ti <sub>2</sub> O <sub>3</sub>		•	-6951
13	Hf	+	8	$Ag(C10_3)$	=	4	Ag <sub>2</sub> Cl	+	12	Hf02	+	HfCl <sub>4</sub>	-6905
2	Th	+		L1(ClO <sub>4</sub> )	=		LiCl	+	2	ThO 2		-	<b>-6750</b>
3	บ	+	2	Na(C10 <sub>3</sub> )	=	2	NaCl	+	3	w <sub>2</sub>			<del>675</del> 0
13	A1	+	6	Ag (C10 <sub>3</sub> )	=	3	Ag <sub>2</sub> Cl	+	6	Al 203	+	AlCl <sub>3</sub>	-6733
16	Ta	+	5	$Mg(C10_4)_2$	==	5	${\rm MgCl}_2$	+	8	Ta2O5		•	-6730
2	υ	+		K(C10 <sub>4</sub> )	=		KCl	+	2	UO 2			67 20
3	Ηf	+	2	$Na(ClO_3)$	=	2	NaCl	+	3	HfO2			6675
8	ri	+	3	Li(ClO <sub>4</sub> )	=	3	LiCl	+	4	Ti 203			6658

Table 22 (cont.)

						Re	eaction	1					Enthalpy, cal/cc
3	Вe	+		K(C103)	=		KCl	+	3	BeO			-6653
2	Н£	+		K(ClO <sub>4</sub> )	=		KCl	+	2	HfO <sub>2</sub>			-6643
3	Ве	+		Rb(ClO <sub>3</sub> )	=		RbC1	+	3	BeO _			-6616
17	Ве	+	4	Ag(C10 <sub>4</sub> )	=	2	Ag <sub>2</sub> Cl	+	16	BeO	+	BeCl <sub>2</sub>	-6573
2	Al	+		Na(ClO3)	=		NaCl	+		A1 <sub>2</sub> 0 <sub>3</sub>		_	-6562
4	Ве	+		Cs(ClO <sub>4</sub> )	=		CsCl	+	4	BeO			-6533
8	Al	+	3	K(ClO <sub>4</sub> )	=	3	KCl	+	4	Al <sub>2</sub> O <sub>3</sub>			<b>-</b> 65 27
10	Zr	+	6	Ag(C10 <sub>3</sub> )	=	3	Ag <sub>2</sub> Cl	+	9	ZrO <sub>2</sub>	+	ZrCl <sub>3</sub>	-6448
8	Ta	+	5	$Li(Clo_4)$	=	5	LiCl	+	4	${\rm Ta_2O_5}$			<del>-</del> 6388
4	U	+		Ba(ClO <sub>4</sub> ) <sub>2</sub>	=		BaCl <sub>2</sub>	+	4	UO <sub>2</sub>			-6292
4	Si	+		$Mg(ClO_4)_2$	=		MgCl <sub>2</sub>	+	4	SiO <sub>2</sub>			<b>-</b> 6289
13	Th	+		$Ag(ClO_3)$	=	4	Ag <sub>2</sub> Cl	+	12	ThO $_2$	+	$\mathtt{ThCl}_4$	-6289
16	МÞ	+	5	$Mg(ClO_4)_2$	=	5	MgCl <sub>2</sub>	+	8	$^{\rm Nb}2^{\rm O}5$			-6249
2	В	+		$Ag(ClO_3)$	=		AgCl	+		B <sub>2</sub> O <sub>3</sub>			-6242
3	Zr	+	2	$Na(ClO_3)$	=	2	NaCl	+	3	ZrO2			-6234
4	Hf	+		$Ba(ClO_4)_2$	=		BaCl <sub>2</sub>	+	4	HfO <sub>2</sub>			-6228
2	Zr	+		K(ClO <sub>4</sub> )	=		KCl	+	2	ZrO <sub>2</sub>			-6192
16	Al	+	3	$Ba(ClO_4)_2$	=		BaCl <sub>2</sub>			A1 203			-6119
3	Th	+	2	$Na(ClO_3)$	=	2	NaCl	+	3	Th $O_2$			-6102
13	Ti	+		Ag (C10 <sub>3</sub> )	=	3	Ag <sub>2</sub> Cl	+	6	Ti <sub>2</sub> O <sub>3</sub>	+	TiCl <sub>3</sub>	-6100
16	Sc	+	3	$Mg(ClO_4)_2$	==	3	MgCl <sub>2</sub>	+		Sc 203			-6099
2	Th	+		K(ClO <sub>4</sub> )	=		KCl	+	2	ThO <sub>2</sub>		•	-6063
2	В	+		$Na(ClO_3)$	=		NaCl	+		B <sub>2</sub> O <sub>3</sub>			-6061
2	U	+		$Rb(ClO_4)$	==		RbC1	+	2				-6040
16	Nd	+	3	$Mg(ClO_4)_2$	=	3	MgCl <sub>2</sub>	+	8	Nd 203			-6036
8	В	+	3	K(C10 <sub>4</sub> )	=	3	KCl	+	4	B203			-6004
2	Si	+		Li(ClO <sub>4</sub> )	==		LiCl	+	2	SiO <sub>2</sub>			-5983
16	La	+	3	$Mg(ClO_4)_2$	=	3	${\rm MgCl}_2$	+	8	La <sub>2</sub> O <sub>3</sub>			-5981
2	Hf	+		Rb(ClO <sub>4</sub> )	=		RbC1	+	2	HfO <sub>2</sub>			-5981
				$Mg(ClO_4)_2$									5980

Table 22 (cont.)

						Re	eaction	1					Enthalpy, cal/cc
16	Pr	+	3	Mg(ClO <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+	8	Pr <sub>2</sub> 0 <sub>3</sub>			-5946
16	Се	+		Mg(C10 <sub>4</sub> ) <sub>2</sub>			MgCl <sub>2</sub>			Ce <sub>2</sub> 0 <sub>3</sub>			-5941
2	Ti	+	•	Na (ClO <sub>3</sub> )	=		NaCl			Ti <sub>2</sub> O <sub>3</sub>			<b>-</b> 5926
8	Мb	+	5	Li(ClO <sub>4</sub> )	=	5	LiCl	+		Nb205			-5914
8	Mg	+		Mg(ClO <sub>4</sub> ) <sub>2</sub>	=		MgCl <sub>2</sub>	+		MgO			-5886
16	Cr	+	3	Mg(ClO <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+	8	Cr <sub>2</sub> 0 <sub>3</sub>			<b>-</b> 5885
8	Sc	+		Li(ClO <sub>4</sub> )	==			+		Sc 203			<b>-</b> 5877
8	Ti	+	3	K(ClO <sub>4</sub> )	=	3	KCl	+		Ti <sub>2</sub> 0 <sub>3</sub>		,	-5876
8	Al	+	3	Rb(ClO <sub>4</sub> )	==	3	RbCl	+		Al <sub>2</sub> 0 <sub>3</sub>			<b>-</b> 5975
8	Nd	+	3	Li(ClO <sub>4</sub> )	=	3	LiCl	+		Nd 203			-5832
4	Zr	+		Ba(C104)2	=		BaCl <sub>2</sub>	+		ZrO <sub>2</sub>			-5817
8	La	+	3	Li(ClO <sub>4</sub> )	=		LiCl	+		La <sub>2</sub> O <sub>3</sub>			-5786
. 3	U	+	2	K(C103)	=	2	KCl	+		vo <sub>2</sub>			<b>-</b> 5779
6	$\mathtt{Ta}$	+	5	Ag(ClO <sub>3</sub> )	=	5	AgCl	+	3	Ta205		·	<b>-</b> 5767
. 8	Pr	+	3	Li(C10 <sub>4</sub> )	=	3	LiCl	+		Pr <sub>2</sub> 0 <sub>3</sub>			~57 <b>47</b>
3	U	+	2	Rb(ClO <sub>3</sub> )	<b>=</b>	2	RbCl	+	3	vo <sub>2</sub>			-5747
13	U	+	6	Ag(ClO <sub>4</sub> )	=	3	Ag <sub>2</sub> C1	+	12	บ0่า	+	ucl <sub>3</sub>	-5747
4	Th	+		Ba(C104)2	=		BaCl <sub>2</sub>	+	4	Tho <sub>2</sub>		•	-5743
8	Ce	+	3	Li(C10 <sub>4</sub> )	=	3	ric1_	+	4	Ce 203			<b>-</b> 573 <b>7</b>
3	Hf	+	2	K(C103)	=	2	KCl	+	3	HfO2			-5728
3	Hf	+	2	Rb(ClO <sub>3</sub> )	=	2	RbCl	+	3	Hf02		ŧ	<b>-</b> 5696
17	Нf	+	8	Ag(ClO <sub>4</sub> )	=	4	Ag <sub>2</sub> Cl	+	16	Hf02	+	$\mathtt{HfCl}_{4}$	-5688
4	Mg	+		Li(ClO <sub>4</sub> )	=		LiCl	+	4	MgO			<b>-</b> 5683
. 8	V	+	3	Li(ClO <sub>4</sub> )	=	3	LiCl	+	4	v <sub>2</sub> o <sub>3</sub>			-5676
2	U	+		Cs(ClO <sub>4</sub> )			CsCl	+	2	υ0 <sub>2</sub>			-5662
2	Al	+		K(C103)	=		KCl	+		Al <sub>2</sub> O <sub>3</sub>			<b>-</b> 5629
2	Hf	+		Cs(ClO <sub>4</sub>	**		CsCl	+	2	HfO2			-5612
. 2	Al	+		Rb(C103)	=		RbCl	+		Al <sub>2</sub> O <sub>3</sub>			<b>-</b> 559 <b>7</b>
6	Ta	+	5	Na(C103)	=		NaCl						<del>-</del> 5596
16	Zr	+	8	Rb(ClO <sub>4</sub> )	=	8	RbCl	+	16	zro <sub>2</sub>			<b>~</b> 5585

Tabl∈ 22 (cont.)

						Re	eaction	J					Enthalpy,
13	Nd	+	6	Ag(C10 <sub>3</sub> )	=	3	Ag <sub>2</sub> Cl	+	6	Nd 203	+	NdCl <sub>3</sub>	-5583
13	Sc	+	6	Ag(C103)	=	3	Ag <sub>2</sub> Cl	+	6	Sc 203	+	ScCl <sub>3</sub>	<del>-</del> 5568
8	Cr	+	3	Li(ClO <sub>4</sub> )	==	3	LiCl	+	4	Cr <sub>2</sub> 0 <sub>3</sub>		Ū	<del>-</del> 5565
16	В	+	3	Ba(ClC) <sub>4</sub>	=	3	BaCl <sub>2</sub>	+	8	B <sub>2</sub> O <sub>3</sub>			<b>-</b> 5562
13	La	+	6	Ag(C10 <sub>3</sub> )	=		Ag <sub>2</sub> Cī			La <sub>2</sub> O <sub>3</sub>	+	$\mathtt{LaCl}_3$	<b>-</b> 5553
17	Al	+	6	$Ag(Clo_4)$	=	3	Ag <sub>2</sub> Cl	+	8	A1 <sub>2</sub> 0 <sub>3</sub>	+	AlCl <sub>3</sub>	<del>-</del> 5553
2	Th	+		Rb(C10 <sub>4</sub> )	=		RbCl	+	2	ThO 2		•	-5542
8	Ta	+	5	K(C104)	=	5	KCl	+	4	Ta 205			-5530
16	Ti	+	3	Ba (C10 <sub>4</sub> ) <sub>2</sub>	=	3	BaCl <sub>2</sub>	+	8	Ti <sub>2</sub> O <sub>3</sub>			<b>-</b> 55 23
13	Ce	+	6	Ag(C10 <sub>3</sub> )	=	3	Ag <sub>2</sub> Cl	+	6	Ce <sub>2</sub> O <sub>3</sub>	+	CeCl <sub>3</sub>	-5514
13	Pr	4	6	Ag(C10 <sub>3</sub> )	=	3	Ag <sub>2</sub> Cl	+	6	Pr <sub>2</sub> 0 <sub>3</sub>	+	PrCl <sub>3</sub>	-5514
8	Al	+	3	Cs(ClO <sub>4</sub> )	=	3	CsCl	+	4	A1 <sub>2</sub> 0 <sub>3</sub>		_	-5512
3	Si	+	2	Ag(C103)	=	2	AgCl	+	3	SiO <sub>2</sub>			-5477
13	Mg	+	4	Ag(C10 <sub>3</sub> )	=	2	Ag <sub>2</sub> Cl	+	12	Mg0	+	MgCl <sub>2</sub>	-5411
6	Nb	+	5	Ag(C10 <sub>3</sub> )	=	5	AgCl	+	3	$Nb_2O_5$		_	-5380
2	Sc	+		Na(C103)	=		NaCl	+		Sc 203			-5379
2	Nd	+		Na(C103)	=		NaCl	+		$Nd_2O_3$			-5374
3	Zr	+	2	K(C103)	=	2	KCl	+	3	ZrO2			<b>-</b> 5363
2	La	+		Na(C103)	=		NaCl	+		La <sub>2</sub> O <sub>3</sub>			<b>-</b> 5350
3	Th	+	2	K(C103)	=	2	KCl	+	3	ThO <sub>2</sub>			-5348
13	Zr	+	6	Ag(ClO <sub>4</sub> )	=	3	Ag <sub>2</sub> Cl	+	12	ZrO <sub>2</sub>	+	· ZrCl <sub>3</sub>	<b>-</b> 5333
3	Zr	+	2	Rb(ClO <sub>3</sub> )	=	2	RbCl	+	3	ZrO <sub>2</sub>		_	-5332
8	Sc	+	3	K(ClO <sub>4</sub> )	=	3	KCl	+	4	Sc 203			-5329
8	Nd	+	3	K(C104)	=	3	KCl	+	4	$Nd_2O_3$			-5327
3	Th	+	2	Rb(C10 <sub>3</sub> )	=	2	RbCl	+	3	ThO <sub>2</sub>			<b>-</b> 5320
				Ag(C10 <sub>4</sub> )							+	$\mathtt{ThCl}_{4}$	~5320
				Na(C103)								•	-5316
2	Pr	+		$Na(ClO_3)$	=		NaCl	+		ProO3			-5307
8	La	+	3	K(C10 <sub>4</sub> )	=	3	KC1	+	4	La <sub>2</sub> 0 <sub>3</sub>			+5305
8	Ti	+	3	$K(ClO_4)$ $Rb(ClO_4)$	=	3	RbCl	+	4	Ti <sub>2</sub> O <sub>3</sub>			-5 299
										· -			

Table 22 (cont.)

							Reaction	on			Enthalpy, cal/cc
2	Се	+		Na(ClO3)	==	-	NaCl	+	Ce <sub>2</sub> O <sub>3</sub>		-5 290
8	В	+	3	Rb(ClO <sub>4</sub> )	=	3	RbCl	+	4 B <sub>2</sub> O <sub>3</sub>		<b>-5 28</b> 9
8	Pr	+		K(C10 <sub>4</sub> )	=	3	KCI	+	4 Pr <sub>2</sub> 0 <sub>3</sub>		<b>-5</b> 259
2	Si	+		K(ClO <sub>4</sub> )	=		KCl	+	2 SiO <sub>2</sub>		-5 247
2	Zr	+		Cs(Clo <sub>4</sub> )	=		CsCl	+	2 ZrO <sub>2</sub>		-5 246
2	Th	+		Cs(ClO <sub>4</sub> )	=		CsCl	+	2 ThO 2		<b>-</b> 5 245
3	Mg	+		Na(ClO3)	=		NaCl	+	3 Mg0		-5 243
8	Ce	+	3	K(C10 <sub>4</sub> )	=	3	KCl	+	4 Ce <sub>2</sub> O <sub>3</sub>		<b>-</b> 5 24 2
9	V	+	4	Ag(ClO <sub>3</sub> )	=	2	Ag <sub>2</sub> Cl	+	4 V <sub>2</sub> O <sub>3</sub> +	VCl <sub>2</sub>	<b>-</b> 5 23 3
6	Мb	+	5	Na(C103)	==	5	NaCl	+	<del>-</del> -	_	<b>-</b> 5 205
4	Mg	+		K(ClO <sub>4</sub> )	==		KCl	+			<b>-51</b> 93
16	Ta	+	5	Ba(ClO <sub>4</sub> ) <sub>2</sub>	=	5	BaCl <sub>2</sub>	+	8 Ta <sub>2</sub> 0 <sub>5</sub>		<b>-515</b> 5
6	Mn	+		$Mg(ClO_4)_2$	=				2 Mn <sub>3</sub> 0 <sub>4</sub>		-5132
L3	Cr	+	6	Ag (C10 <sub>3</sub>	=	3	Ag <sub>2</sub> Cī		6 Cr <sub>2</sub> O <sub>3</sub> +	CrCl <sub>3</sub>	-5129
8	Мb	+	5	K(C10 <sub>4</sub> )	=	5	KCI	+	<del>-</del> -		-5128
2	Ti	+		K(C103)	=		KCl	+	Ti <sub>2</sub> O <sub>3</sub>		-5095
L6	Nd	+	3	Ba(C10 <sub>4</sub> ) <sub>2</sub>	=	3	BaCl <sub>2</sub>	+			<b>-</b> 5086
16	La	+	3	Ba(ClO <sub>4</sub> ) <sub>2</sub>	=	3	BaCl <sub>2</sub>	+	8 La <sub>2</sub> 0 <sub>3</sub>	•	<del>-</del> 5074
16	Sc	+		Ba(C10 <sub>4</sub> ) <sub>2</sub>	=				8 Sc 203		-5071
2	ίΤ	+		Rb(ClO <sub>3</sub> )	=		RbC1	+	Ti <sub>2</sub> O <sub>3</sub>		<b>-</b> 5065
2	V	+		Na(C103)	=		NaCl	+	v <sub>2</sub> 0 <sub>3</sub>		-5054
2	В	+		K(ClO <sub>3</sub> )	=		KCl	+	B <sub>2</sub> O <sub>3</sub>	•	-5046
L7	Ti	+	6	Ag(C10 <sub>4</sub> )	==	3	Ag <sub>2</sub> Cl	+	8 Ti <sub>2</sub> O <sub>3</sub> +	TiCl <sub>3</sub>	-5041
				Ba(C10 <sub>4</sub> ) <sub>2</sub>						· ·	-5026
				Rb(ClO <sub>3</sub> )							-5010
				Ba(C10 <sub>4</sub> ) <sub>2</sub>							-5005
				K(ClO <sub>4</sub> )							-4978
				Cs(ClO <sub>4</sub> )							-4977
				Ba(C10 <sub>4</sub> ) <sub>2</sub>							-4960
8	В	+	3	Ag(ClO <sub>4</sub> )	<b></b>	3	AgCl	+	4 B <sub>2</sub> O <sub>3</sub>		-4941

Table 22 (cont.)

		<b>.</b>				Rea	ction	······					Enthalpy, cal/cc
2	Cr	+		Na(ClO <sub>3</sub> )	=		NaCl	+		Cr <sub>2</sub> O <sub>3</sub>			<b>-</b> 4933
8	W	+	3	Mg(ClO <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+	8	wo <sub>3</sub>			<b>-</b> 4928
8	Nd	+		Rb(ClO <sub>4</sub> )	=		RbCl			Nd 203			-4922
4	Si	+		Ba(ClO4)2	=	-	BaCl <sub>2</sub>	+	4	SiO <sub>2</sub>			-4921
8	La	+	3	Rb(ClO <sub>4</sub> )	=	3	RbCl			La <sub>2</sub> 0 <sub>3</sub>			-4916
8	Ta	+	5	Rb(ClO <sub>4</sub> )	=	5	RbCl	+	4	Ta 205			-4912
8	В	+		Cs(ClO <sub>4</sub> )	=	3	CsCl	+	. 4	B <sub>2</sub> O <sub>3</sub>			<b>-</b> 4905
8	Sc	+	3	Rb(ClO <sub>4</sub> )	=	3	RbCl	+	4	Sc 203			-4896
8	Pr	+	3	$Rb(ClO_4)$	=.	.3	RbCl	+	4	Pr <sub>2</sub> 0 <sub>3</sub>			-4866
8	Cr	+	3	K(C10 <sub>4</sub> )	=	3	KCl	+	.4	Cr <sub>2</sub> O <sub>3</sub>			-4851
8	Ce	+	3	$Rb(ClO_4)$	<b>=</b> ,	3	RbC1	+	4	Ce 203			-4843
3	Mn	+		$Li(Clo_4)$	=		LiCl	+		$^{\mathrm{Mn}_3\mathrm{O}_4}$			-4839
17	La	+		$Ag(ClO_4)$	<b>=</b> .	3	${\rm Ag_2Cl}$	.+	8	$La_2O_3$	+	$LaCl_3$	-4803
17	Nd	+	6	$Ag(ClO_4)$	= .	. 3	${\rm Ag_2Cl}$	+	3	Nd 203			-4802
4	Mg	+		$Rb(ClO_4)$	=		RbCl	+	4	MgO			<b>-</b> 4799
16	Nb	+	5	Ba(C10 <sub>4</sub> ) <sub>2</sub>	=	5	BaCl <sub>2</sub>	+	8	$Nb_2O_5$			-4786
2	Nd	+		K(C103)	=		KCl	+		$^{\rm Nd}2^{\rm O}3$			<b>-</b> 4783
2	La	+		K (C10 <sup>3</sup> )	=		KC1	+		$La_2O_3$			-4782
2	La	+		Rb(ClO <sub>3</sub> )	==		RbCl	+		$La_2O_3$			-4759
2	Nd	+		$Rb(Clo_3)$	=		RbCl	+	-	$^{\text{Nd}}_{2}^{\text{O}_{3}}$			-4759
17	Pr	+	6	$Ag(ClO_4)$	=	3	${\rm Ag_2Cl}$	+	8	$Pr_2O_3$	+	PrCl <sub>3</sub>	-4854
2	Sc	+		K(C10 <sub>3</sub> )	=		KCl	+	•	Sc 203			-4749
17	Sc	+	6	$Ag(ClO_4)$	==	3	${\rm Ag_2Cl}$	+	8	Sc 203	+	ScCl <sub>3</sub>	-4745
17	Ce	+	6	$Ag(ClO_4)$	=	3	Ag <sub>2</sub> Cl	+	8	Ce <sub>2</sub> O <sub>3</sub>	+	CeCl <sub>3</sub>	-4739
2	Pr	+		K(C10 <sup>3</sup> )	=		KCl	+		Pr <sub>2</sub> 0 <sub>3</sub>			-4732
				$Rb(ClO_3)$									-4724
6	Ta	+	5	K (C10 <sup>3</sup> )	=	5	KCl	+	3	Ta 205			-4713
				Rb(ClO <sub>3</sub> )									-4709
16	Ga	+	3	$Mg(ClO_4)_2$	=	3	MgCl <sub>2</sub>	+	8	Ga 203			-4708
2	Ce	+		K(C10 <sup>3</sup> )	=		KCl			Ce <sub>2</sub> O <sub>3</sub>			-4708
2	Si.	+		$Rb(ClO_4)$	=		RbCl	+	2	$sio_2$			-4701

Table 22 (cont.)

***						Re	action	1					Enthalpy, _cal/cc
8	La	+	3	Cs(ClO <sub>4</sub> )	=	3	CsC1	+	4	La <sub>2</sub> O <sub>3</sub>			-4691
				$Cs(ClO_{\Lambda}^{3})$			CsCl			Nd 203			-4689
	Ce			· · · · · · · · · · · · · · · · · · ·	=		RbCl			Ce <sub>2</sub> O <sub>3</sub>			-4685
6	Ta	+	5	Rb(ClO <sub>3</sub> )	=	5	RbCl	+	3				-4679
16	V	+	3	Ba(C10 <sub>4</sub> ) <sub>2</sub>	=	3	BaCl <sub>2</sub>	+	8	v <sub>2</sub> o <sub>3</sub>			-4670
3	Mg	+		K(ClO <sub>3</sub> )	=		KCl	+	3	Mg0			-4666
17	Mg	+	4	Ag(C10 <sub>4</sub> )	=	2	Ag <sub>2</sub> Cl	+	16	Mg0	+	${ t MgCl}_2$	-4661
8	Sc	+	3	Cs(ClO <sub>4</sub> )	=	3	CsCl	+	4	Sc <sub>2</sub> 0 <sub>3</sub>			-4648
3	Mg	+		Rb(C103)	=		RbCl	+	3	MgO			-4643
8	Pr	+	3	Cs(ClO <sub>4</sub> )	=	3	CsCl	+	4	Pr <sub>2</sub> 0 <sub>3</sub>			-4639
13	Mn	+	4	Ag(C10 <sub>3</sub> )	=	2	Ag <sub>2</sub> Cl	+	12	MnO	+	MnCl <sub>2</sub>	-4626
8	Ta	+	5	Ag(C10 <sub>4</sub> )	=	5	AgC1	+	4	Ta <sub>2</sub> 0 <sub>5</sub>			-4626
8	Ce	+	3	Cs(ClO <sub>4</sub> )	=	3	CsCl	+	4	Ce <sub>2</sub> O <sub>3</sub>			-4614
4	W	+	3	Li(ClO <sub>4</sub> )	=	3	LiCl	+	4	wo <sub>3</sub>			-4587
8	Ta	+	5	Cs(ClO <sub>4</sub> )	=	5	CsCl	+	4	Ta <sub>2</sub> O <sub>5</sub>			-4577
4	Mg	+		Cs(C10 <sub>4</sub> )	=		CsCl	+	4	MgO			-4572
	ďИ			Rb(ClO <sub>4</sub> )	=	5	RbCl	+	4	Nb205			-4554
16	Çr	+	3	Ba(C104) 2	=	3	BaCl <sub>2</sub>	+	8	Cr <sub>2</sub> O <sub>3</sub>			-4539
3	Si	+	2	K(C103)	=	2	KCl	+	3	sio <sub>2</sub>			-45 29
3	Sı	+	2	Rb(ClO <sub>3</sub> )	=	2	RbC1	+	3	Sio_2			-4498
8	V	+	3	Rb(C10 <sub>4</sub> )	=	3	RbCl	+	4	v <sub>2</sub> 0 <sub>3</sub>			-4455
8	Ga	+	3	Li(ClO <sub>4</sub> )	=	3	LiCl	+	4	Ga <sub>2</sub> O <sub>3</sub>		•	-4454
2	Si	+		Ag(ClO <sub>4</sub> )	=		AgCl	+	2	SiO <sub>2</sub>			-4454
8	Мо	+	3	Mg(ClO <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+	8	McO3			_4449

Table 23

MOST ENERGETIC CHLORATE AND PERCHLORATE REACTIONS WITH METALS,
IN TERMS OF GRAVIMETRIC ENTHALPY

						F	Reactio	n.						Enthalpy,
4	Ве	+		Li(ClO <sub>4</sub> )	=		LiCl	+		BeO				-4037
8	Ве	+			=		MgCl <sub>2</sub>	+	8	BeO				-3998
16	Li	+		$Mg(ClO_4)_2$	=		Mg0	+	7	Li <sub>2</sub> O	+	2	LiCl	-3576
8	Li	+			==		LiCl	+	4	Li <sub>2</sub> 0				-3463
3	Ве	+		$Na(ClO_3)$	=		NaCl	+	3	BeO				-3374
4	Ве	+		K (C10 <sub>4</sub> )	=	•	KCl	+	4	BeO				-3348
34	Li	+	2	Cu (ClO <sub>4</sub> ) <sub>2</sub>	=		Cu <sub>2</sub> 0	+	15	Li <sub>2</sub> 0	+	4	LiCl	-3323
12	Li	+		Li(ClO <sub>3</sub> )	=		Li <sub>2</sub> 0	+	5	Li <sub>2</sub> 0	+	2	LiCl	-3310
16	Li	+	2	$Na(ClO_4)$	=		Na <sub>2</sub> O	+	7	Li <sub>2</sub> 0	+	2	LiCl	-3110
26	Li	+	2	Cu (C10 <sub>3</sub> ) <sub>2</sub>	=		Cn <sup>2</sup> 0	+	11	Li <sub>2</sub> 0	+	4	LiCl	-3015
3	Ве	+		K(C103)	=		KCl	+	3	BeO				-2999
6	Li	+		Na(ClO <sub>3</sub> )	=		NaCl	+	3	Li <sub>2</sub> 0				<b>-</b> 2969
8	Li	+		K(ClO4)	=		KCl	+	4	Li <sub>2</sub> 0				- 2937
8	Al	+	3	Li(ClO <sub>4</sub> )	=	3	LiCl	+	4	Al <sub>2</sub> 0 <sub>3</sub>				-2934
16	Al	+	3	$Mg(ClO_4)_2$	=	3	MgCl <sub>2</sub>	+	8	Al <sub>2</sub> 0 <sub>3</sub>				<b>~2933</b>
8	В	+		Li(ClO <sub>4</sub> )	=	3	LiCl	+	4	B203				-2912
16	В	+		$Mg(ClO_4)_2$	=	3	MgCl <sub>2</sub>	+	8	B <sub>2</sub> O <sub>3</sub>				-2912
8	Ве	+		Ba (ClO <sub>4</sub> ) 2	=		BaCl <sub>2</sub>	+	8	Be0				-2891
8	Mg	+		$Mg(ClO_4)_2$	=		MgCl <sub>2</sub>			MgO				- 2784
4	Mg	+		Li(ClO <sub>4</sub> )	=		LiCl	+	4	MgO			•	-2782
6	Li	+		K(C103)	=		KCl	+	3	Li <sub>2</sub> 0				<del>-</del> 2666
4	Ве	+		Rb(C10 <sub>4</sub> )	=		RbCl	+	4	BeO				-2638
16	Li	+		Ba(C10 <sub>4</sub> ) <sub>2</sub>	=		BaCl <sub>2</sub>	+	8	Li <sub>2</sub> 0				<b>-</b> 25 7 5
2	Al	+		Na (C103)			NaCl	+		A1203				<b>- 2565</b>
				Ag(ClO <sub>4</sub> )									BeCl <sub>2</sub>	- 2533
				K(ClO <sub>4</sub> )			KCl						••	<b>-</b> 25 3 0
				Mg(ClO <sub>4</sub> ) <sub>2</sub>			MgCl <sub>2</sub>							-2486
3	Mg	+		Na(C103)	=									-2474
				Li(ClO <sub>4</sub> )										- 2473

Table 23 (cont.)

. 2004 - 1004					<del>-1</del>	I	Reactio	n					<del></del>	Enthalpy, cal/q
2	В	+		Na(ClO <sub>3</sub> )	=		NaCl	+		B <sub>2</sub> O <sub>3</sub>				- 2455
4	Mg	+		K(C101)	=		KCl	+		MgO				-2442
8	В	+	3	K(ClO <sub>4</sub> )	=	3	KCl	+	4	B <sub>2</sub> O <sub>3</sub>			•	-2408
16	Sc	+	3	Mg(ClO <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+						- 2394
8	Sc			Li(ClO <sub>4</sub> )	=		LiCl							-2383
8	Li	+		Rb(ClO <sub>4</sub> )	=		RbCl							-2364
17	Li	+	2	Ag (C10 <sub>4</sub> )	=		Ag <sub>2</sub> Cl	+	8	Li <sub>2</sub> 0	+		LiCl	-2351
2	Al	+		K(C103)	=		KCI	+		A1 <sub>2</sub> 0 <sub>3</sub>				- 23 21
3	Ве	+		Rb(ClO <sub>3</sub> )	=		RbCl	+	3	BeO				-2281
3	Mg	+		K(C103)	=		KC1	+	3	MgO				-2261
8	Ca	+		Mg(ClO <sub>4</sub> ) <sub>2</sub>	=		MgCl <sub>2</sub>	+	8	CaO				-2257
4	Ca			Li(ClO <sub>4</sub> )	=		LiCl	+	4	CaO				-2245
16	Al	+	3	Ba (C10 <sub>4</sub> ) 2	=	3	BaCl <sub>2</sub>	+	8	Al 203				-2242
14	Al	+	2	Cu(ClO <sub>4</sub> ) <sub>2</sub>	=		cu <sub>2</sub> o_	+	5	Al 203	+	4	AlCl	-2234
	Li			Ba (ClO <sub>3</sub> ) 2			BaO	+	5	Li <sub>2</sub> 0	+	2	LiCl	-2217
8	Mg	+		Ba (C10 <sub>4</sub> ) <sub>2</sub>	=		BaCl <sub>2</sub>	+	8	MgO				-2191
4	Ве	+		Cs(ClO <sub>4</sub> )	==		CsCl	+	4	BeO		•		-2174
2	В			K(C103)	=		KCl	+		B <sub>2</sub> O <sub>3</sub>				-2168
13	Ве	+	4	Ag (C10 <sub>3</sub> )	==	2	Ag <sub>2</sub> Cl	+	12		+		BeCl <sub>2</sub>	-2167
3	Si	+	2	Na (ClO <sub>3</sub> )	=	2	MaCl	+	3	SiO <sub>2</sub>			-	-2157
2	Sc	+		Na (ClO3)	=		NaCl	+		sc 203				-2156
8	Sc	+	3	K(C104)	=	3	KCl	+		Sc 203			•	-2122
2	Si	+		K(C104)	=		KC1	+		sio <sub>2</sub>				-2112
14	В	+	2	Cu (C10 <sub>4</sub> ) 2	==		Cu <sub>2</sub> O	+	5	B203				-2083
				Ba (C104) 2			-							- 2076
				Mg(C10 <sub>4</sub> ) <sub>2</sub>										-2071
				Rb(ClO <sub>3</sub> )										-2071
8	Al	+	3	Rb(ClO <sub>4</sub> )	==	3	RbC1	+	4	Al <sub>2</sub> O <sub>3</sub>				- 2067
				Na (C103)										- 2065
				Ag (ClO <sub>3</sub> )							+	1	LiCl	- 2054
				L1 (C104)										- 2053

Table 23 (cont.)

						F	Reactio	n						Enthalpy,
4	Mg	+		Rb(ClO <sub>4</sub> )	=		RbCl	+	4	MgO				<b>-</b> 2035
4	Ca	+		K(C10 <sub>4</sub> )	=		KCl	+	4	CaO				-2034
20	Al	+	6	Na(ClO <sub>4</sub> )	=	3	$Na_2O$	+	7	Al <sub>2</sub> 0 <sub>3</sub>	+	6	AlCl	-2015
17	Mg	+	4	Ag(C10 <sub>4</sub> )	=	2	Ag <sub>2</sub> Cl	+	16	MgO	+		MgCl <sub>2</sub>	-2000
17	Al	+	6	Ag(ClO <sub>4</sub> )	=	3	Ag <sub>2</sub> Cl	+	8	Al <sub>2</sub> O <sub>3</sub>	+		AlCl <sub>3</sub>	-1999
2	Sc	+		K(C103)	=		KCI			Sc <sub>2</sub> O <sub>3</sub>			_	-1984
34	Ве	+	4	Cu (ClO <sub>4</sub> ) <sub>2</sub>	=	2	Cu <sub>2</sub> O	+	15	BeO	+	4	BeCl <sub>2</sub>	-1978
16	Al	+	6	Li(ClO <sub>3</sub> )	=	3	Li <sub>2</sub> O	+	5	Al <sub>2</sub> O <sub>3</sub>	+	6	AlCl	-1977
8	Li	+		Cs(ClO <sub>4</sub> )	=		CsCl	+	4	Li <sub>2</sub> 0				-1977
12	Ве	+	4	Li(ClO <sub>3</sub> )	=	2	Li <sub>2</sub> 0	+	5	БеО	+	2	BeCl <sub>2</sub>	-1935
3	Si	+	2	K(ClO <sub>3</sub> )	=	2	KCl	+	3	${ m SiO}_2$			_	<b>-</b> 1935
16	Sc	+	3	Ba(C10 <sub>4</sub> ) <sub>2</sub>	=	3	BaCl <sub>2</sub>	+	8	Sc 203				-1924
	Ca			K(C103)			KCl	+	3	CaO				-1920
34	Al	+	6	Cu (ClO <sub>3</sub> ) <sub>2</sub>	=	3	Cu <sub>2</sub> C	+	11	A1203	+	12	AlCl	-1903
ક	В	+	3	Rb(ClO <sub>4</sub> )	=	3	RbC1	+	4	B203				-1878
2	Ti	+		Na(ClO3)	=		NaCl	<b>,</b>		Ti 203				-1876
8	Ça	+		Ba(C10 <sub>4</sub> ) <sub>2</sub>	=		BaCl <sub>2</sub>	+	8	CaO				-1869
4	Si	+		Ba(C104) 2	=		BaCl <sub>2</sub>	+	4	SiO <sub>2</sub>				-1959
8	Ti	+	3	K(C!O4)	=	3	KC1	+	4	Ti 203				-1839
2	Al	+		Rb(C103)	=		RbC1	Ť		Al 203				-1831
3	Mg	+		Rb(C103)	=		RbC1	+	3	MgO				-1821
8	В	+	3	Ag (C104)	<b>=</b>	3	AgC1	+	4	B <sub>2</sub> O <sub>3</sub>				-1800
8	Sc	*	3	Rb(C10 <sub>4</sub> )	=	3	RbC1	+	4	3c 203			•	-1794
20	В	+	6	Na (C10 <sub>4</sub> )	=	3	Na <sub>2</sub> O	+				5	BCl	-1793
4	Zr	+		Mg(C104) 2	==		MgCl <sub>2</sub>	+	4	ZiO2				-1777
13	Mg	+	4	Ag(C103)	==	2	Ag <sub>2</sub> Cl	+	12	MgO	+		MgCl <sub>2</sub>	-1773
26	Ве	+	4	Cu (C103) 2	=	2	Cu <sub>2</sub> O	+	11	BeO	+	4	BeCl <sub>2</sub>	-1771
17	Sc	+	6	Ag (C104)	=	3	Ag <sub>2</sub> Cl	+	8	Sc 203	+		Sc 203	-1770
16	В	+	6	Li(ClO <sub>3</sub> )	=	3	Li <sub>2</sub> 0	+	5	B203	÷	6	BCI	-1758
				Li(ClO <sub>4</sub> )										-1758
4	Ca	+		Rb(ClO <sub>4</sub> )	<b>22</b>		RbC1	+	4	O <sub>E</sub> O				-1757

Table 23 (cont.)

						Re	eaction	<u>1</u>						Enthalpy, cal/q
17	Ca	+	4	Ag(ClO <sub>4</sub> )	=	2	Ag <sub>2</sub> Cl	+	16	CaO	+		CaCl <sub>2</sub>	-1754
13	Al	+	6	Ag (C103)	≠ .	3	Ag <sub>2</sub> Cl	+	6	Al <sub>2</sub> 0 <sub>3</sub>	+		AlCl <sub>3</sub>	-1747
8	Al	+	3	Cs(ClO <sub>4</sub> )	=	3	CsCl	+	4	Al <sub>2</sub> 0 <sub>3</sub>			•	-1747
4	Mg	+		Cs(ClO <sub>4</sub> )	=		CsCl	+	4	MgO				-1744
16	Ве	+	4	Na(C10 <sub>4</sub> )	=	2	$Na_2O$	+	7	BeO	+	2	BeCl <sub>2</sub>	-1729
2	Ti	+		K(C103)	=		KCl	+		Ti <sub>2</sub> 0 <sub>3</sub>			_	-1729
2	Si	+		Rb(C10 <sub>4</sub> )	=		RbCl			SiO <sub>2</sub>				-1699
34	В	+	6	Cu (C10 <sub>3</sub> ) <sub>2</sub>	=	3	Cu <sub>2</sub> O	+	11	B <sub>2</sub> O <sub>3</sub>	+	12	BCl	-1682
16	Ti	+	3	Ba (C104) 2	=	3	BaCl <sub>2</sub>	+	8	Ti <sub>2</sub> O <sub>3</sub>				-1675
2	Si	+		Ag(C10 <sub>4</sub> )	=		AgCl	+	2	SiO2				-1644
3	Zr	+	2	Na(C103)	=	2	NaCl	+	3	ZrO2				-1643
2	В	+		Rb(ClO <sub>3</sub> )	=		RbCl	+		B <sub>2</sub> O <sub>3</sub>				-1632
2	Sc	+		Rb(C103)	=		RbCl	+		Sc 203				-1622
2	Zr	+		K(ClO <sub>4</sub> )	=		KCl	+	2	ZrO2				-1610
3	Ca	Ť		Rb(ClO <sub>3</sub> )	=		RbCl	+	3	CaO				-1607
13	Ca	+	4	Ag(C10 <sub>3</sub> )	=	2	Ag <sub>2</sub> C1	+	12	Ca0	+		CaCl <sub>2</sub>	-1594
16	V	+	3	$Mg(ClO_4)_2$	=	3	MgCl <sub>2</sub>	+	8	$v_2o_3$			-	-1588
13	Sc	+	6	Ag (C10 <sub>3</sub> )	==	3	Ag <sub>2</sub> Cl	+	6	sc 203	+		ScCl <sub>3</sub>	-1584
8	Ti	+	3	Rb(C10 <sub>4</sub> )	=	3	RbC1	+	4	Ti203			<b>*</b>	-1561
8	V	+	3	Li(ClO <sub>4</sub> )	=	3	LiCl	+	4	v <sub>2</sub> 0 <sub>3</sub>				-1560
8	Sc	+	3	Cs(ClO <sub>4</sub> )	=	3	CsCl	÷	4	Sc 203				-1554
4	Ca	+		Cs(C10 <sub>4</sub> )	=		CsCl	+	4	CaO			•	-1546
8	В	+	3	Cs(C104)	=	3	CsCl	+	4	B203				-1540
3	Zr	+	2	к(сто <sup>3</sup> )	=	2	KC1	+	3	zro <sub>2</sub>				-1534
2	В	+		Ag (C10 <sub>3</sub> )	=		AgC1	+		B203				-1533
17	Ti	+	6	Ag(C10 <sub>4</sub> )	n	3	Ag <sub>2</sub> C1	+	8	Ti <sub>2</sub> O <sub>3</sub>	+		TiCl <sub>3</sub>	-15 28
				Rb(C103)									-	-1502
4	Zr	+		Ba(C104)2	=		BaCl <sub>2</sub>	+	4	$zro_2$				-1491
34	Mg	+	4	Cu(C104)2	=	2	Cu <sub>2</sub> 0	+	30	MgO	+	4	MgCl <sub>2</sub>	-1478
12	Mg	+	4	ri(c103)	3	2	Li <sub>2</sub> 0	+	10	MgO	+	2	MgCl <sub>2</sub>	-1470

Table 23 (cont.)

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	nalpy, L/g
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	162
16 Nb + 5 Mg(ClO <sub>4</sub> ) = 5 MgCl + 8 Nb <sub>2</sub> O <sub>5</sub> -14  12 Na + 2 Li(ClO <sub>3</sub> ) = Li <sub>2</sub> O + 5 Na <sub>2</sub> O + 2 NaCl -14  18 Na + 2 Mg(ClO <sub>4</sub> ) = 2 MgO + 7 Na <sub>2</sub> O <sub>2</sub> + 4 NaCl -14  34 Na + 2 Cu(ClO <sub>4</sub> ) = Cu <sub>2</sub> O + 15 Na <sub>2</sub> O + 4 NaCl -14  4 C + Mg(ClO <sub>4</sub> ) = MgCl <sub>2</sub> + 4 CO <sub>2</sub> -14  8 Cr + 3 Li(ClO <sub>4</sub> ) = 3 LiCl + 4 Cr <sub>2</sub> O <sub>3</sub> -14  3 Si + 2 Ag(ClO <sub>3</sub> ) = 2 AgCl + 3 SiO <sub>2</sub> -14  2 Si + Cs(ClO <sub>4</sub> ) = CsCl + 2 SiO <sub>2</sub> -14  2 Ti + Rb(ClO <sub>3</sub> ) = RbCl + Ti <sub>2</sub> O <sub>3</sub> -14  8 V + 3 K(ClO <sub>4</sub> ) = 3 KCl + 4 V <sub>2</sub> O <sub>3</sub> -14  8 V + 3 K(ClO <sub>4</sub> ) = 3 RbCl + 16 ZrO <sub>2</sub> -14  16 Al + 3 Ba(ClO <sub>3</sub> ) = 2 Cu <sub>2</sub> O + 22 MgO + 4 MgCl <sub>2</sub> -14  26 Na + 2 Cu(ClO <sub>3</sub> ) = Cu <sub>2</sub> O + 11 Na <sub>2</sub> O + 4 NaCl -15  26 Na + 2 Cu(ClO <sub>3</sub> ) = Cu <sub>2</sub> O + 11 Na <sub>2</sub> O + 4 NaCl -15  3 Ti + 6 Ag(ClO <sub>4</sub> ) = 3 CsCl + 4 Ti <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 3 Cs(ClO <sub>4</sub> ) = 3 CsCl + 4 Ti <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 3 Cs(ClO <sub>4</sub> ) = 3 CsCl + 4 Ti <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 6 Ag(ClO <sub>3</sub> ) = NaCl + Ti <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 6 Ag(ClO <sub>3</sub> ) = NaCl + Cr <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 6 Ag(ClO <sub>3</sub> ) = NaCl + Cr <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 6 Ag(ClO <sub>3</sub> ) = NaCl + Cr <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 3 Cs(ClO <sub>4</sub> ) = 3 CsCl + 4 Ti <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 6 Ag(ClO <sub>3</sub> ) = NaCl + Cr <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 6 Ag(ClO <sub>3</sub> ) = NaCl + Cr <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 6 Ag(ClO <sub>3</sub> ) = NaCl + Cr <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -15  8 Ti + 7 Cs(ClO <sub>3</sub> ) = 7 Na <sub>2</sub> O <sub>3</sub> + 7 Na <sub>2</sub> O <sub>3</sub> + 7 Na <sub>2</sub> O <sub>3</sub> + 11  16 Na + 2 Na(ClO <sub>4</sub> ) = Na <sub>2</sub> O <sub>3</sub> + 7 Na <sub>2</sub> O <sub>3</sub> + 2 NaCl -15  18 Na + 4 Li(ClO <sub>4</sub> ) = 2 Li <sub>2</sub> O <sub>3</sub> + 7 Na <sub>2</sub> O <sub>3</sub> + 4 NaCl -15  18 Na + 4 Li(ClO <sub>4</sub> ) = 2 Li <sub>2</sub> O <sub>3</sub> + 7 Na <sub>2</sub> O <sub>3</sub> + 4 NaCl -15  16 Mg + 4 Na(ClO <sub>4</sub> ) = 2 Na <sub>2</sub> O <sub>3</sub> + 14 MgO + 2 MgCl <sub>2</sub> -15	<del>1</del> 51
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	148
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	146
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	145
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	143
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	133
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	132
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	125
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	122
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	120
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	119
16 Al + 3 Ba(ClO <sub>3</sub> ) <sub>2</sub> = 3 BaO + 5 Al <sub>2</sub> O <sub>3</sub> + 6 AlCl -13 26 Mg + 4 Cu(ClO <sub>3</sub> ) <sub>2</sub> = 2 Cu <sub>2</sub> O + 22 MgO + 4 MgCl <sub>2</sub> -13 26 Na + 2 Cu(ClO <sub>3</sub> ) <sub>2</sub> = Cu <sub>2</sub> O + 11 Na <sub>2</sub> O + 4 NaCl -13 13 Zr + 6 Ag(ClO <sub>4</sub> ) = 3 Ag <sub>2</sub> Cl + 12 ZrO <sub>2</sub> + ZrCl <sub>3</sub> -13 2 C + Li(ClO <sub>4</sub> ) = LiCl + 2 CO <sub>2</sub> -13 13 Ti + 6 Ag(ClO <sub>3</sub> ) = 3 Ag <sub>2</sub> Cl + 6 Ti <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -13 8 Ti + 3 Cs(ClO <sub>4</sub> ) = 3 CsCl + 4 Ti <sub>2</sub> O <sub>3</sub> -13 2 Cr + Na(ClO <sub>3</sub> ) = NaCl + Cr <sub>2</sub> O <sub>3</sub> -13 2 V + K(ClO <sub>3</sub> ) = KCl + V <sub>2</sub> O <sub>3</sub> -13 2 V + K(ClO <sub>3</sub> ) = 5 NaCl + 3 Nb <sub>2</sub> O <sub>5</sub> -13 16 Na + 2 Na(ClO <sub>4</sub> ) = 2 Li <sub>2</sub> O + 7 Na <sub>2</sub> O <sub>2</sub> + 4 NaCl -13 18 Na + 4 Li(ClO <sub>4</sub> ) = 2 Li <sub>2</sub> O + 7 Na <sub>2</sub> O <sub>2</sub> + 4 NaCl -13 16 Mg + 4 Na(ClO <sub>4</sub> ) = 2 Na <sub>2</sub> O + 14 MgO + 2 MgCl <sub>2</sub> -1	111
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	103
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	398
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	382
$ 2 C + Li(ClO_4) = LiCl + 2 CO_2                                 $	381
13 Ti + 6 Ag(ClO <sub>3</sub> ) = 3 Ag <sub>2</sub> Cl + 6 Ti <sub>2</sub> O <sub>3</sub> + TiCl <sub>3</sub> -1 8 Ti + 3 Cs(ClO <sub>4</sub> ) = 3 CsCl + 4 Ti <sub>2</sub> O <sub>3</sub> -1 2 Cr + Na(ClO <sub>3</sub> ) = NaCl + Cr <sub>2</sub> O <sub>3</sub> -1 2 V + K(ClO <sub>3</sub> ) = KCl + V <sub>2</sub> O <sub>3</sub> -1 6 Nb + 5 Na(ClO <sub>3</sub> ) = 5 NaCl + 3 Nb <sub>2</sub> O <sub>5</sub> -1 16 Na + 2 Na(ClO <sub>4</sub> ) = Na <sub>2</sub> O + 7 Na <sub>2</sub> O + 2 NaCl -1 18 Na + 4 Li(ClO <sub>4</sub> ) = 2 Li <sub>2</sub> O + 7 Na <sub>2</sub> O <sub>2</sub> + 4 NaCl -1 16 Mg + 4 Na(ClO <sub>4</sub> ) = 2 Na <sub>2</sub> O + 14 MgO + 2 MgCl <sub>2</sub> -1	379
$8 \text{ Ti} + 3 \text{ Cs}(\text{ClO}_4) = 3 \text{ CsCl} + 4 \text{ Ti}_2\text{O}_3 -1$ $2 \text{ Cr} + \text{ Na}(\text{ClO}_3) = \text{ NaCl} + \text{ Cr}_2\text{O}_3 -1$ $2 \text{ V} + \text{ K}(\text{ClO}_3) = \text{ KCl} + \text{ V}_2\text{O}_3 -1$ $6 \text{ Nb} + 5 \text{ Na}(\text{ClO}_3) = 5 \text{ NaCl} + 3 \text{ Nb}_2\text{O}_5 -1$ $16 \text{ Na} + 2 \text{ Na}(\text{ClO}_4) = \text{ Na}_2\text{O} + 7 \text{ Na}_2\text{O} + 2 \text{ NaCl} -1$ $18 \text{ Na} + 4 \text{ Li}(\text{ClO}_4) = 2 \text{ Li}_2\text{O} + 7 \text{ Na}_2\text{O}_2 + 4 \text{ NaCl} -1$ $16 \text{ Mg} + 4 \text{ Na}(\text{ClO}_4) = 2 \text{ Na}_2\text{O} + 14 \text{ MgO} + 2 \text{ MgCl}_2 -1$	376
$2 \text{ Cr} + \text{Na}(\text{ClO}_3) = \text{NaCl} + \text{Cr}_2\text{O}_3 \qquad -1$ $2 \text{ V} + \text{K}(\text{ClO}_3) = \text{KCl} + \text{V}_2\text{O}_3 \qquad -1$ $6 \text{ Nb} + 5 \text{ Na}(\text{ClO}_3) = 5 \text{ NaCl} + 3 \text{ Nb}_2\text{O}_5 \qquad -1$ $16 \text{ Na} + 2 \text{ Na}(\text{ClO}_4) = \text{Na}_2\text{O} + 7 \text{ Na}_2\text{O} + 2 \text{ NaCl} \qquad -1$ $18 \text{ Na} + 4 \text{ Li}(\text{ClO}_4) = 2 \text{ Li}_2\text{O} + 7 \text{ Na}_2\text{O}_2 + 4 \text{ NaCl} \qquad -1$ $16 \text{ Mg} + 4 \text{ Na}(\text{ClO}_4) = 2 \text{ Na}_2\text{O} + 14 \text{ MgO} + 2 \text{ MgCl}_2 \qquad -1$	369
$2 V + K(ClO_3) = KCl + V_2O_3 -1$ $6 Nb + 5 Na(ClO_3) = 5 NaCl + 3 Nb_2O_5 -1$ $16 Na + 2 Na(ClO_4) = Na_2O + 7 Na_2O + 2 NaCl -1$ $18 Na + 4 Li(ClO_4) = 2 Li_2O + 7 Na_2O_2 + 4 NaCl -1$ $16 Mg + 4 Na(ClO_4) = 2 Na_2O + 14 MgO + 2 MgCl_2 -1$	357
$6 \text{ Nb} + 5 \text{ Na}(\text{ClO}_3) = 5 \text{ NaCl} + 3 \text{ Nb}_2\text{O}_5 \qquad -1$ $16 \text{ Na} + 2 \text{ Na}(\text{ClO}_4) = \text{Na}_2\text{O} + 7 \text{ Na}_2\text{O} + 2 \text{ NaCl} \qquad -1$ $18 \text{ Na} + 4 \text{ Li}(\text{ClO}_4) = 2 \text{ Li}_2\text{O} + 7 \text{ Na}_2\text{O}_2 + 4 \text{ NaCl} \qquad -1$ $16 \text{ Mg} + 4 \text{ Na}(\text{ClO}_4) = 2 \text{ Na}_2\text{O} + 14 \text{ MgO} + 2 \text{ MgCl}_2 \qquad -1$	340
$6 \text{ Nb} + 5 \text{ Na}(\text{ClO}_3) = 5 \text{ NaCl} + 3 \text{ Nb}_2\text{O}_5 \qquad -1$ $16 \text{ Na} + 2 \text{ Na}(\text{ClO}_4) = \text{Na}_2\text{O} + 7 \text{ Na}_2\text{O} + 2 \text{ NaCl} \qquad -1$ $18 \text{ Na} + 4 \text{ Li}(\text{ClO}_4) = 2 \text{ Li}_2\text{O} + 7 \text{ Na}_2\text{O}_2 + 4 \text{ NaCl} \qquad -1$ $16 \text{ Mg} + 4 \text{ Na}(\text{ClO}_4) = 2 \text{ Na}_2\text{O} + 14 \text{ MgO} + 2 \text{ MgCl}_2 \qquad -1$	339
18 Na + 4 Li(ClO <sub>4</sub> ) = 2 Li <sub>2</sub> O + 7 Na <sub>2</sub> O <sub>2</sub> + 4 NaCl -1 16 Mg + 4 Na(ClO <sub>4</sub> ) = 2 Na <sub>2</sub> O + 14 MgO + 2 MgCl <sub>2</sub> -1	332
18 Na + 4 Li(ClO <sub>4</sub> ) = 2 Li <sub>2</sub> O + 7 Na <sub>2</sub> O <sub>2</sub> + 4 NaCl -1 16 Mg + 4 Na(ClO <sub>4</sub> ) = 2 Na <sub>2</sub> O + 14 MgO + 2 MgCl <sub>2</sub> -1	317
$16 \text{ Mg} + 4 \text{ Na}(\text{ClO}_4) = 2 \text{ Na}_2\text{O} + 14 \text{ MgO} + 2 \text{ MgCl}_2$ -1	306
	301
	299
· · · · · · · · · · · · · · · · · · ·	296
2	29 2

Table 23 (cont.)

						I	Reactio	on				and the second s	Enthalpy, cal/g
16	V	+	3	Ba(ClO <sub>4</sub> ) <sub>2</sub>	=				8	V 203	-		-1 29 2
				Mg(ClO <sub>4</sub> ) <sub>2</sub>			_						-1 280
				Li(ClO <sub>3</sub> )	=		Li <sub>2</sub> 0				+	2 CaCl <sub>2</sub>	-1274
8	La	+	3	Li(ClO <sub>4</sub> )	=	3	LiCl	+	4	La <sub>2</sub> 0 <sub>3</sub>		-	-1262
34	Ca	+	4	Cu (ClO <sub>4</sub> ) <sub>2</sub>			Cu <sub>2</sub> O					4 CaCl <sub>2</sub>	-1260
10	Zr			$Ag(ClO_3)$		3	Ag <sub>2</sub> Cl	+	9	ZrO2	+	$ZrCl_3$	-1257
2	Zr	+		Cs(ClO <sub>4</sub> )	=		CsCl	+	2	zro2		J	-1244
2	Cr	+		K(C103)	=	•	KCl	+		Cr <sub>2</sub> O <sub>3</sub>			-1237
8	Sr	+		Mg(ClO <sub>4</sub> ) <sub>2</sub>			MgCl <sub>2</sub>	+	8				-1235
8	Na	+		K(ClO <sub>4</sub> )			KCl	+	4	Na <sub>2</sub> O			-1234
3	C			$Na(ClO_3)$		2	NaCl						-1233
6	Nb	+	5	K(C103)	=	5	KCl	+	3	Nb <sub>2</sub> O <sub>5</sub>			-1233
16	Pr	+	3	$Mg(ClO_4)_2$									~1229
12	Ве	+		Ba (C103) 2			BaO				+	2 BeCl 2	-1225
2	La	+		Na(ClO <sub>3</sub> )	=		NaCl	+		La <sub>2</sub> 0 <sub>3</sub>		••	-1224
б	Mn	+		$Mg(ClO_4)_2$	=		MgCl <sub>2</sub>	+	2	$Mn_3O_4$			-1221
4	Sr	+		Li(ClO <sub>4</sub> )			LiCl	+	4	SrO			-1216
26	Сą	+	4	Cu (ClO <sub>3</sub> ) <sub>2</sub>	=	2	Cu <sub>2</sub> O	*	22	CaO	+	4 CaCl <sub>2</sub>	-1214
				Li(ClO <sub>4</sub> )		3	Lici	+	4	Pr <sub>2</sub> 03		~	-1211
16	Ce	+	3	Mg (C10 <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+	8	Ce <sub>2</sub> O <sub>3</sub>			-1208
	٧			Rb(ClO <sub>4</sub> )	<b>=</b>		RbCl	+	4	$v_2 o_3$			-1202
16	Nd	+	3	Mg(C10 <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+	8	Nd 203		•	-1200
8	La	+		K(ClO <sub>4</sub> )		3	KCI	+	4	La <sub>2</sub> O <sub>3</sub>			-1200
16	Cr	+		Ba (C10 <sub>4</sub> ) 2									-1192
8	Ce	+	3	Li(ClO <sub>4</sub> )	22	3	LiC1	+	4	Ce <sub>2</sub> O <sub>3</sub>			-1190
3	Mn	+		Li(ClO <sub>4</sub> )	=		LiCl	+		Mn <sub>3</sub> O <sub>4</sub>			-1190
16	Иb	+	5	Ba(C10 <sub>4</sub> ) <sub>2</sub>	=	5	BaCl <sub>2</sub>	+	8	Nb205			-1189
6	Na	+		K(C103)	==		KCl	+	3	Na <sub>2</sub> O			-1185
				$Ag(ClO_4)$							+	3 VCl <sub>2</sub>	-1183
8	Мď	+	3	L1 (C104)	2	3	LiCl	+	4	Ng og		•	-1182
				Na (Clo3)									-1179

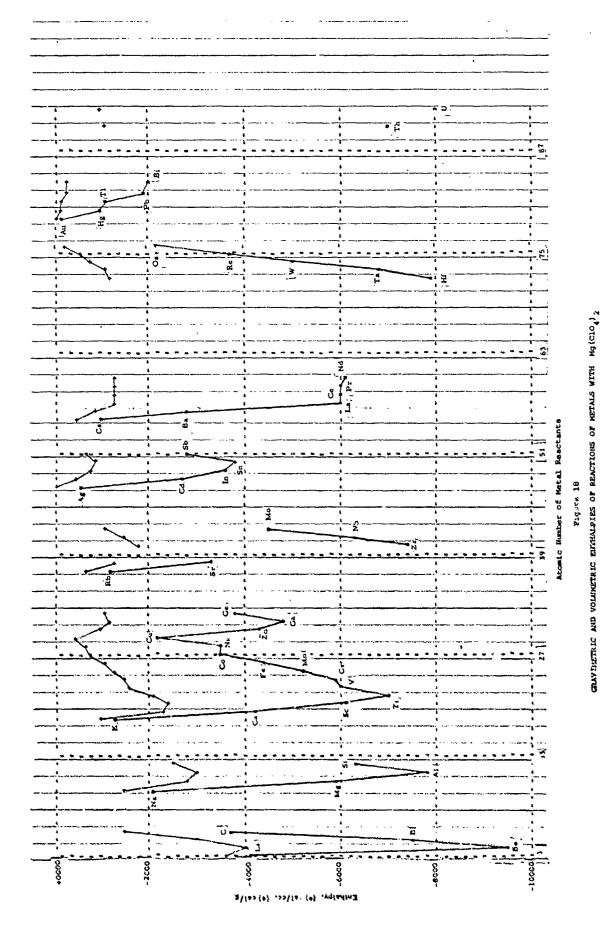
Table 23 (cont.)

						]	Reactio	on					Enthalpy, cal/q
16	Ga	+	3	Mg(C10 <sub>4</sub> ) <sub>2</sub>	=	3	MgCl <sub>2</sub>	+	8	Ga <sub>2</sub> O <sub>3</sub>			-1177
2	Pr	+		$Na(Clo_3)$	==		NaCl	+		Pr <sub>2</sub> 0 <sub>3</sub>			-1176
4	Hf	+		Mg(ClO <sub>4</sub> ) <sub>2</sub>	==		MgCl <sub>2</sub>	+	4	H£0 <sub>2</sub>			-1172
2	La	+		K(C103)	=		KCl _	+		La <sub>2</sub> 03			-1170
2	C	+		K (C104)	==		KCl	*	2	co <sub>2</sub>			-1160
2	Се	+		Na(ClO <sub>3</sub> )	==		NaCl	+		Ce <sub>2</sub> O <sub>3</sub>			-1157
4	Sr	+		K(C10 <sub>4</sub> )	==		KCl	+	4	Sr0			-1155
2	Hf	+		Li(ClO <sub>4</sub> )	=		Licl	+	2	HfO <sub>2</sub>			-1153
8	Pr	+	3	$K(ClO_4)$	72	3	KCl	+	4	Pr <sub>2</sub> 0 <sub>3</sub>			-1153
2	Nd	+		$Na(ClO_3)$	=		NaC1	+		Nd 203			-1150
8	Ga	+	3	$Li(ClO_4)$	==	3	LiCl	+	4	Ga <sub>2</sub> O <sub>3</sub>			-1147
16	La	+	3	$Ba(ClO_4)_2$	=	3	BaCl <sub>2</sub>	+	8	La <sub>2</sub> 03			-1145
8	Сe	+	3	$K(Clo_4)$	=	3	KCI	+	4	Ce <sub>2</sub> O <sub>3</sub>			-1133
8	Nd	+	3	$K(Clo_4)$	=	3	KCl	+	4	$100^{20}$			-1127
16	Ca	+	4	$Na(ClO_4)$	=	2	Na <sub>2</sub> O	+	7	CaG	+	2 CaCl <sub>2</sub>	-1125
2	Pr	+		K(C10 <sup>3</sup> )	=		KCl	+		Pr <sub>2</sub> 03			1125
3	Sr	+		K(C10 <sup>3</sup> )	=		KCl	*	3	Sr0			-1125
3	Hf	+	2	Na(ClO <sub>3</sub> )	=	2	NaCl	+	3	$^{\rm HfO}_2$			-1121
16	В	+	3	Ba (C103) 2	=	3	BaO	+	5	B <sub>2</sub> O <sub>3</sub>	+	6 BCI	-1116
12	Na	+		Ba (C103) 2	=		PaO	4-	5	Na20	+	2 NaCl	-1112
8	Çr	+	3	Rb(ClO <sub>4</sub> )	=	3	RbC1	+	4	cr <sub>2</sub> o <sub>3</sub>			-1108
8	Ир	+	5	Rb(C10 <sub>4</sub> )	=	5	RbC1	+	4	Nb205		,	-1107

Table 24

CHLORATES AND PERCHLORATES
IN DESCENDING ORDER OF HEAT OF REACTION

Volumetric Heat of Reaction	Gravimetric Heat of Reaction
$Mg(ClO_4)_2$	$Mg(ClO_4)_2$
LiClO <sub>4</sub>	LiClO <sub>4</sub>
AgClO <sub>3</sub>	NaClO3
NaClO <sub>3</sub>	KClO <sub>4</sub>
KC104	KC103
$Ba(ClO_4)_2$	Ba(C10 <sub>4</sub> ) <sub>2</sub>
RbClO <sub>4</sub>	$RbClO_4$
KC103	$\mathtt{AgClO}_{4}$
RbClO <sub>3</sub>	RbClO3
AgClO <sub>4</sub>	AgC103
CsClO <sub>4</sub>	CsClO <sub>4</sub>
	Cu (C104) 2
	Cu (ClO <sub>3</sub> ) 2
	Liclo <sub>3</sub>
	$Ba(Clo_3)_2$



ASD\_TDR-63-846

The plot in Figure 19 presents the data in a different manner. The volumetric enthalpies for the reactions of all the chlorates and perchlorates with beryllium are plotted. This allows one to choose an oxidizer for a particular metal reactant, beryllium in this case. Lithium perchlorate is the best oxidizer, and the alkali metal perchlorates follow a decreasing trend in enthalpy in progressing to cesium perchlorate. The gravimetric enthalpies, shown in Figure 20, exhibit similar trends.

The volumetric and gravimetric enthalpies of all 801 chlorate and perchlorate reactions are summarized in Tables 25 and 26, respectively. The same trends noted previously are apparent here.

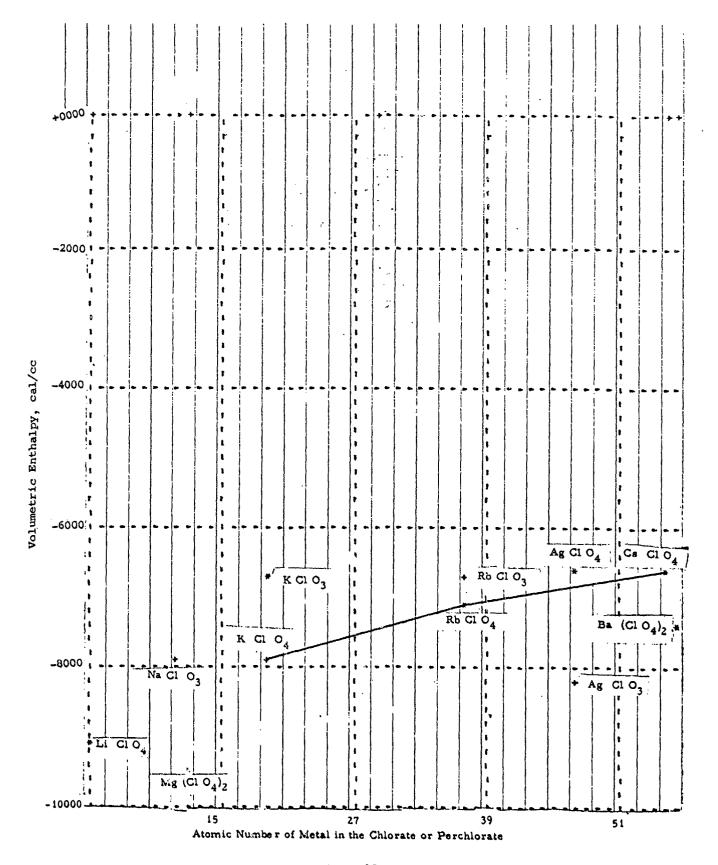


Figure 19

VOLUMETRIC ENTHALPIES OF REACTIONS
OF CHLORATES AND PERCHLORATES WITH Be

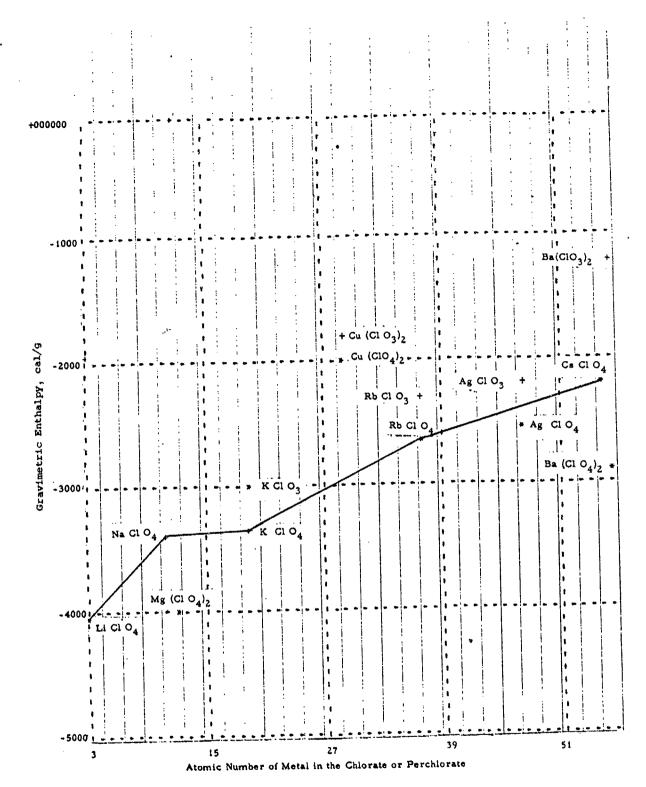


Figure 20 GRAVIMETRIC ENTHALPIES OF REACTIONS OF CHLORATES AND PERCHLORATES WITH Be

Table 25

VOL'UMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CHLORATES AND PERCHLORATES (In descending order from top to bottom and left to right)

	Mg (C10 <sub>4</sub> ) <sub>2</sub>	. 7 . 61.0	AgClO <sub>3</sub>	NaCIO -	кс104	B= (C10 )	RbClO <sub>4</sub>	KC10.~	ъс10 <sub>3</sub>	·AqClO,	CsC10 <sub>4</sub>
		-L1C10 <sub>4</sub>		1140103		Ba(C10 <sub>4</sub> / <sub>2</sub>	2	3		6570	6533
BE.			-0103	-1000						-6578 -5847	-6533 -5662
U	-7989	-7670	-6989	-6750	-6720	-6292	-6040 -5981	-5//9	-3/4/ 5606	-5688	-5612
_HF	7874		-6905	-6675	-6643	-6228	-2281	-5629	5597	-5553	-5512
AL	-7742	-7431	-6733	-6562	-6527	-6119 -5562	5289	5046	5010	-4941	-4905
_B _			-6242	-6061	-6004			-5363		-5333	-5246
ZR	-7318	-7021	-6448	-6234	-6192 -6063	-5817 -5743	-5542	_5348	-5320	-5320	-5245
	6998 .		-6289	-6102 -5926	-5876	-5523	-5299	-5095		-5041	-4977
TI	-6951	-6658	-6100 -5767	-5596 -5596	-5530	-5155		-4713		-4626	-4577
	-6730 - -6289	-5983	-5477	-5316	-5247	-4291		-4529		-4454	-4401
SI	-6269 6249			-5205	-5128	-4786	4554			-4307	-4243
SC.	-6099	-5877	-5568	-5379	-5329	-5071	-4896	-4749	-4724	-4745	-4648
		-5832	<b>-</b> 5583	-5374	-5327	-5086	-4922	-4783	<b>-4759</b>	-4802	-4689
LA	-5981	-5786	-5553	-5350	-5305	-5074	-4916	-4782	-4759	-4803	-4591
		-5676			-4978	-4670	-4455	-4300	-4269	-4263	-4169
PR	-5946	-5747	-5514	-5307	-5259	-5026	-4866	-4732	-4709	-4754	-4639
	5941_		-5514	-5290	-5242	-5005	-4866 -4843	-4708	-4685	4739	-4614
MG	-5886	-5683	-5411	-5243	-5193	<b>~4960</b>	-4799	-4666	-4643	-4661	-4572
CR	5885	5565	-5129	4933	-4851		-4319	-4167	-4136	4130	4031
MN	-5132	-4839	-4626	-4395	-4310				-3758	-3804	-3662
W	-4928	4587	-4276	-4080	-3965		-3489	-3392	-3359		3239
GA		-4454	-4230	-4075	-3984		-3600	-3514	-3488	-3478	-3391
. MO	4449	-4115	-3896	-3697	-3569		-3138				-2928 -2946
FE	-4337	-4038	-3852	-3669	-3551		-3155	-3090	~3001	-3065 -3237	-3121
ZN	4262	4029		3731	-3637		-3303	-3240	2560	-3606	-3504
CA		-4068	-4031	-3891	-3839		-3628	-3576 -3347	~3330	-3396	-3275
		3796	-3804	-3642	-3597			-2832		-2818	-2706
SN		-3521	-3441	-3283	-3175					-2763	-2642
	3753			3247	-3131		4011	-2531	-2500	-2526	-2371
RE		-3329	-3264	-3058	-2910		2513	-2494	-2463	-2491	-2331
C	3628	3295	-3236	-3025	-2873 -3066			-2766		-2756	= = = = =
IN		-3360	-3310 -3172	-3166 -3001	-2878			-2559	-2533	-2555	-2423
NI		-3206 -3164	-3135	-2948	-2815		_2524	-2507	-2481	-2508	-2371
CO SR		-3112	-3159	-3029	-2976			-2819		-2862	~2755
SB		-2561	-2625	-2468	-2347			-2135		-2144	-2010
BA		-2615	-2701	-2571	-2520			-240B		-2462	-2350
CI		-2451	-2521	-2385	-2280				-2083	-2123	
, Cu		1935	-2105	-1930	-1784		1597	-1644	-1619	-1670	
OS		-1902		-1902	-1732	21665	-1524	-1582	-1555	-1614	
N.		-1323		-1698	-1627	7 -1663			-1574		
81		-1742		-1761	-1649		-1516	-1556	-1537	-1579	
PE		1720	-1855	-1739	-1641				-1543	-1580	
K	-1299	-1080	-1245	-1068	-971		-931			-1072	
RE		912		-910	-7e7		-727				
TI	_1092	-884	-1033	-945	-87	•	-825				
H					-764		-697				
CS	-911	-752					-606				
, A	_107	629					803 -193				
AC	-523	-190	-460	-329	-21	7 –248	-193	-204	-2/0	-334	-103

Table 26

GRAVIMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CHLORATES AND PERCHLORATES (In descending order from top to bottom and left to right)

Mg(ClO <sub>4</sub> ) <sub>2</sub>	NaCIO3	KC103	RbC10 <sub>4</sub>	RbC103	CsC	.O <sub>4</sub> C1	1(ClO <sub>3</sub> ) <sub>2</sub>	NaClO <sub>4</sub>	
Lich		Ba(C10	AgCl		AgClO <sub>3</sub>	Cu(C104)	, Li	ClO <sub>3</sub> Ba	(C10 <sub>3</sub> ),
BE - 3008 -403	73374 -3348	~2999 -289	-2618 -ZE.	33 -2541.	-2167 -21	74 -1978	-1771 -1	1935 -1729	-1225
LI =3576 =346	3 -2960 -2017	-2665 -2575	5 →2364 <u>-23</u> !	51 -2071	-2054 -1q	77 -3324	-3015 -3	011E- 01F	-2217
AL =2933 =293 _B =2912 =291	4 -2564 -2440	-2321 -2743	2 -2067 -199	99 -1831	-1747 -17	47 -2234	-190 -1	1977 -2015	
MG -2784 -278	.224554408  224782885	-2241 -2191	1 -2035 -200	30 -1831 30 -1034	-1773 -17	44 -1478	-1485 -1		-1116 -1032
_512486247	3 -2157 -2112	-1935 -1859	-1699 -164	14 -1502	-1425 -14	22 -707	•	-650 -479	-403
SC -2394 -238	3 -2154 -2122	-1984 -1924	-1794 -177	70 -1622	-1594 -15	54 -048		-050 -787	-676
CA -2257 -224	5 -2064 -2034	1920 -1869	-1757 -175	54 -160/	-1594 -15	46 -1260	. •	1274 -1125	-957
TI -2071 -205						-	-817 -	-935 -736	-634
4R=1777 =179								-e70 -781	-672
CR: -1462 -143	0 -1451 -1411	-1339 -1294	-1203 -116	13 -1104				789 -677	<b>-</b> g74
	9 -1337 -1202				-972 -0 -979 -9		. • .	706 =600 262 =167	-511
NA -1445 -130				31 -1001			- ·	•262 -167 1446 -1317	-171 -1112
	6 -1233 -1140				°731 ≈7			125 3	34
LA -1280 -126				2 -1045				539 -453	-444
SP -1235 -121				2 -1001	-1013 -0	67 -722		733 -641	-605
				-	-10019		- 4513 -	·510 -434	-426
MN -1221 -119		~967 ~965			-450 mg			412 °514	<b>-π</b> φ8
CE: +1208 +119					-996 -9			410 -430	-424
NO =1200 =118 					=990 =9 ==54 =A			K04 -422	-416
HF -1172 -115			-1000 +95	-	-932 -4			480 <b>-703</b>	-538 -409
FE_ =103099					-729 -6			403 -317	#3U1
KO -1030 -98		-771 -833	, .		-713 -6			370 -30n	-200
th +1025 =100	8 -991 -070	953 -933	-69F 469	5 -864	-450 -A			333 -266	-2/6
GE =1074 =98		-877 -839		-	-723 -4	78 -17	27	62 82	72
TA:101299		.=914 <del>+8</del> 5/			-7947			417 -375	-328
K ∾997 ≈95 U ≈929 ≈91:		-782 -801 -866 -846			-665 -6	-		625 -836	-765
U92991:		-816 -78V		*	-765 -7 -703 -6			357 <u>-300</u>	-201
		-768 -752		•	-723 -A			744 -722	-404 -404
SN -813 -79		-728 -70U			-610 -5			373 +310	-24C
# -76875	7 -734 -409	690 <del>-</del> 663		-	-600 -a			257 -21A	-197
CO =750 =71		-608 -582		9 -522	-442 -4	97 -18a	-364 -	352 -260	-502
IN72569		662636	.,		97 5			F30 17	-449
NI -620 -659		-622 -595 -560 -535			443 44			754 -272	-203
Sa -620 -59 Ra -620 -52		-560 -535			-495 -4 -468 -3			181 -117 1170 -117	-175
RE -558 -52		-507 -482		-	+451 -4			127 -64	-413
CS -452 -37		-335 -350			+345 -2			312 -275	-283
CU=411=39		-389 -366		_	-155 -1			245 -204	-201
CO -445 -42	2 -439 -414	~420 ~404	~382 <b>-</b> 40	0 -3/8	-197 -5	56 -204		548103	-201
" AI " -500 " -500		-274 -264			-256 -2			135 -131	-112
CS -265 -23		-254 -23/	-217 +24		-246 -2			-91 -50	_03
PB =248 =21		225 -216			-552 -1		• •	129 -95	. <b>₩</b> 108
TL -115 -9;		-101 -96 -104 -95	-9) #10 -86 #10			39 -110	• •	104 -87	· _94
HG -101 -8		دو هه دو هه	_			93 -67 90 18		38 -26	-40 46
	5 -44 -29	-42 -34	-26 -4	•	•	70 18 26 <b>-</b> ⊅5	72 -44	30 72 442 <b>413</b>	٥٤ــ
and years	· · · · · · · · · · · · · · · · · · ·	•							

## I. Chloride Reactions

The computer was used to examine 10,545 reactions involving 102 chlorides. and 3061 of these reactions were printed. As a class, the chloride reactions are not especially energetic. The highest enthalpy recorded was only -3336 cal/cc, for the reaction of cerium with rhenium pentachloride. The chloride reactions are less energetic than the fluoride, oxide, chlorate, perchlorate, nitrate, nitrite, chromate, and silicide reactions.

The computer output for some of the more energetic reactions is shown in Table 27. Molybdenum and tungsten chlorides behave as some of the better oxidizers in the chloride systems. The reactions of molybdenum pentachloride, tungsten pentachloride, and tungsten hexachloride with various metals are included in the table.

The most energetic reactions are presented in Tables 28 and On a volumetric basis the most effective metal reducing equats are the rare earths (cerium, lanthanum, praseodymium, neodymium, thorium, and uranium), the rare earth predecessors (yttrium and scandium), the alkali metals (lithium), the alkaline earth metals (beryllium, magnesium, and calcium), and hafnium and zirconium. Beryllium is not the most energetic reducing agent in the chloride systems, because the heat of formation of beryllium chloride is comparatively low. The heats of formation of the alkali earth chlorides increase monotonically, while the heats of formation of the alkalis with oxides exhibit a maximum at calcium. The chlorides increase from -122 to -205 kcal/mole from beryllium to barium: and the oxides increase from -146 to -151 kcal/mole from beryllium to calcium and then decrease to -133 kcal/mole at barium. The behavior of beryllium in the chloride systems may be considered normal and its behavior in the oxide systems anomalous. Its effectiveness in the oxide systems compared with the other alkaline earth metals is thus due to the relatively high heat of formation of the oxide. In addition, because of its low atomic volume and weight, it is still an effective reducing agent in the chloride systems, although it is exceeded in efficacy by several other metals including calcium and magnesium. The most effective oxidizers on a volumetric basis are rhenium pentachloride, hexachloroethane, tungsten tetrachloride, tungsten pentachloride, and tungsten hexachloride.

On a gravimetric basis the alkali metals (lithium, sodium, and potassium) are the most effective reducing agents, followed by the alkaline earth metals (calcium, magnesium, and beryllium), the rare earth predecessors (scandium and yttrium), and titanium. The alkali metals are relatively energetic on a gravimetric basis, and are much less energetic on a volumetric basis because of their extremely low densities. The most effective practical oxidizers on a gravimetric basis are the chlorides of carbon

Table 27

DATA ON VARIOUS REACTIONS OF METALS WITH CHLORIDES

	5 Ba	+ 2 MoC1 <sub>5</sub> ==	2 Mo	+ 5 BaCl <sub>2</sub>
Heat of formation Molecular weight	137.36	_90.80 273.24	٥	-205.56 208.27
Density Melting point, oc	3.50 704.00 3638.00	2.93 194.00 268.00	10,20 2610.00 4800.00	962.00 1189.00
Boiling point, "C Heat of reaction, kcal Reactants' density	-846.20 3.22 -686.14			
Gravimetric enthalpy, cal/c	-2210,16			
The same of the sa	5 Be	+ 2 MoCl <sub>5</sub> =	2 Mo	+ 5 BeCl <sub>2</sub>
Heat of formation	0 0		ני	-122,30
Molecular Weight	1.85		10,	7,9
Melting point, °C	1283.00	194.00 268.00	2610.00 4800.00	00
Bolling point, 'C' Heat of reaction, kcal	4 29 5 90			
H TO	7.26.74 -726.74 -2037.45			
,			- 100 (00) (00) (00) (00) (00) (00)	
- مطاوعي المن فصير مستمدرات فصمة . و م رعال مستم ! م همد لها دست و مستمده همه ومه نماز معدمة ومستمد عمل مد ر	5 Bi	4 MOCL <sub>5</sub>	4 MO	5 BiCl4
Heat of formation	06 806	90 . 80 273 . 24	10	-120,00 350,83
Molecular Weight Density	9,80	2.93	10,20 2610,00	225,00
Melting point, "C Boiling point, "C	14 20 . 00	263.00	à	
Heat of Agation, Kcal	236 <sub>=</sub> 80 4 : 45			
Reactants Persic Gravine Cravinetric enthalpy, cal/g Volumetric enthalpy, cal/cc	-110,76 493 43			

Table 27 (cont.)

e de la martinage est est est est est est est est est es	5 Mg +	2 MoCl <sub>E</sub> =	2 Mo +	5 MgCl <sub>2</sub>
Heat of formation Molecular veight Density Melting point, "C Boiling point, "C Heat of reaction, keal Reactants' density Gravimetric enthalpy, cal/g	1 4 6 40 60	273.24 273.24 2.93 194.00 268.00	95.95 10.20 2610.00 4800.00	-153.40 95.23 2.32 714.00 1415.00
	5 Mn +	2 MoCl <sub>5</sub> =	2 Mo +	5 MnCl <sub>2</sub>
Heat of form tion Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, al/cc	54.94 7.20 1.244.00 2087.00 -394.90 -480.39	-90.80 273.24 2.93 194.00 268.00	95.95 10.20 2610.60 4800.00	-115.30 125.84 2.98 650.00 1190.00
	S Na +	MoCl <sub>5</sub> =	Mo +	. 5 NaCl
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	22.99 .97 .97 98.00 889.00 -400.36 1.83 -1031.34	_90.80 273.24 2.93 194.00 268.00	95.95 10.20 2610.00 4800.00	-98.23 53.45 2.16 808.00 1465.00

Table 27 (cont.)

	5 Ba +	2 WCl <sub>5</sub>	= 2 W	+	5 BaCl <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	137.36 3.50 704.00 1638.00 -859.80 3.68 -610.12	-84.00 361.21 3.88 248.00 276.00	183.8 19.3 380.0 5900.0	86 00 00	-205.56 208.27 962.00 1189.00
	5 Be +	2 WC1 <sub>5</sub>	= 2 W	+	5 BeCl <sub>2</sub>
Heat of formation Molecular weight Dersity Melting point, °C Boiling point, °C Heat of reaction, kral Reactants' density Gravimetric enthalpy, cal/g	9.01 1.85 1.283.00 2970.00 -443.50 3.64 -577.86	-84.00 361.21 3.88 248.00 276.00	183.6 19.3 380.0 5900.0	886 00 00 00	-122.30 79.93 1.90 405.00 547.00
	5 Bi +	4 WCl <sub>5</sub>	= 4 W	+	5 Bicl4
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	208,99 9,80 271,00 1420,00 -254,00 5,19 -106,03 -550,59	_84.00 361,21 3,83 248,00 276,00	183.8 19. 380° 5900°	86 00 00	-120°00 350.83 225.00

Table 27 (cont.)

Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g -709.76						7
	1.32 1.74 0.00 0.00 0.00 3.29 5.96	-84,00 361,21 3,88 248,00 276,00		183,86 19,30 380,00 5900,00	-15 9 71 141	3,40 2,33 4,00 8,00
2 Mn	An +	2 WC1 <sub>5</sub>	11	2 W	+ 5 N	MnC1 <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g -409.6	4.94 7.20 4.00 7.00 8.50 4.44 8.92	-84.00 361.21 3.88 248.00 276.00		183.86 19.30 380.00 5900.00	-11. 12. 65. 119.	5.30 5.84 2.98T 0.00
5 Na	Na +	WCl5	li	M	4 5 h	NaCl
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g -855.0 Volumetric enthalpy, cal/c -1923.0	2.99 .97 9.00 7.16 5.08 5.08	-84.00 361.21 3.88 248.00 276.00		183.86 19.30 380.00 5900.00	146	-98.23 58.45 2.16 808.00 465.00

Table 27 (cont.)

	2 La	+	WC1 6	u	W	+	2 LaCl <sub>3</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	138.92 6.15 880.00 1800.00 -428.50 -635.29		-98.70 396.66 3.52 284.00. 336.50		183.86 19.30 380.00 5900.00		-263.60 245.29 3.84 870.00
	6 L1	+	WC1 <sub>6</sub>	tt.	W	+	6 L1C1
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	6.94 .53 180.00 1326.00 -487.50 -1112.25		-98.70 396.66 3.52 284.00F 336.50		183.86 19.30 380.00 5900.00		-97.70 42.40 2.07T 610.00 1382.00
	3 Mg	+	WC1 <sub>6</sub>	ш	W	+	3 MgCl <sub>2</sub>
Heat of formation 'Molecular weight Density Melting point, 'C Boiling point, 'C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/g	24.32 1.74 650.00 1120.00 -361.50 3.04 -769.77		-98,70 396,66 3,52 284,00 336,50		163.86 19.30 380.00 5900.00		-153.40 95.23 2.32 714.00 1418.00

Table 28

MOST ENERGETIC CHLORIDE REACTIONS WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

				Rea	ctic	n				Enthalpy,
5	Се	+	3	ReCl <sub>5</sub>	=	3	Re	+	5 CeCl <sub>3</sub>	-3336
5	La	+	3	ReCl <sub>5</sub>	=	3	Re	+	5 LaCl <sub>3</sub>	-3301
5	Pr	+	3	ReCl <sub>5</sub>	=	3	Re	+	5 PrCl <sub>3</sub>	<b>-32</b> 59
5	ьи	+	3	ReCl <sub>5</sub>	=	3	Re	+	5 NdCl3	-3244
5	Y	+	3	ReCl <sub>5</sub>	=	3	Re	+	5 YC1 <sub>3</sub>	-3178
2	Се	+		C2Cl6	=	2	C	+	2 CeCl <sub>3</sub>	-3047
2	La	+		C2C16	=	2	C	+	2 LaCl <sub>3</sub>	-3025
5	Lı	+		ReCl <sub>5</sub>	=		Re	+	5 LiCl	-3006
5	Ū	+	3	ReCl <sub>5</sub>	==	3	Re	+	5 UC1 <sub>3</sub>	<b>-29</b> 86
2	Pr	+		C2Cl6	=	2	C	+	2 PrCl <sub>3</sub>	<b>- 29</b> 86
2	Nd	+		C2Cl6	==	2	C	+	2 NdCl <sub>3</sub>	-2970
5	Ca	+	2	ReCl <sub>5</sub>	==	2	Re	+	5 CaCl <sub>2</sub>	-2916
5	Hf	+	3	ReCl <sub>5</sub>	===	3	Re.	+	5 HfCl3	<b>- 28</b> 99
2	Y	+		C <sub>2</sub> Cl <sub>6</sub>	=	2	C	+	2 YC13	<b>- 2</b> 897
5	Mg	+	2	ReCl <sub>5</sub>	=	2	Re	+	5 MgCl <sub>2</sub>	-2872
5	Sc	+	3	ReCl <sub>5</sub>	722	3	Re	+	5 ScCl <sub>3</sub>	-2860
5	Th	+	4	ReCl <sub>5</sub>	=	4	Re	+	5 ThCl <sub>4</sub>	<b>- 28</b> 59
5	Zr	+	3	ReCl <sub>5</sub>	==	3	Re	+	5 ZrCl <sub>3</sub>	- 28 24
6	Li	+		c2c16	<b>322</b>	2	С	· <b>}</b>	6 LiCl	-2814
4	Ce	+	3	WCl <sub>4</sub>	和	3	W	4.	4 CeCl <sub>3</sub>	- 2807
4	La	+		WCl <sub>4</sub>	=	3	W	+	4 LaCl <sub>3</sub>	- 2788
4	Pr	+	3	WCl <sub>4</sub>	23.	3	W	+	4 PrCl <sub>3</sub>	-2745
3	Ca	+		<sup>C</sup> 2 <sup>Cl</sup> 6	m	2	С	+	3 CaCl <sub>2</sub>	-2735
5	Ce	+	3	WCl <sub>5</sub>	==	3	W	+		-2731
2	Ce	+		MCT <sup>6</sup>	=		M	+	2 CeCl <sub>3</sub>	-2730
5	Вe	*	2	ReCl <sub>5</sub>	=	2	Re	+	5 BeCl <sub>2</sub>	- 27 29
4	Nd	*	3	WCl <sub>4</sub>	<b>#</b>	3	W	+	4 NdCl <sub>3</sub>	-2726
2	V	+		C2C16	23	2	C	+	2 UC1 <sub>3</sub>	<b>- 27 2</b> 5
- 5	La	÷	3	WC15	Ħ	3	W	+		-2715

Table 28 (cont.)

		Reac	tion	1			Enthalpy, cal/cc
2 La	+	WC16	=	W	+	2 LaCl <sub>3</sub>	-2714
5 Sr	+	2 ReCl <sub>5</sub>	=	2 Re	+	5 SrCl <sub>2</sub>	-2682
5 Ce	+	3 MoCl <sub>5</sub>	==	3 Mo	+	5 CeCl <sub>3</sub>	-2676
5 Pr	+	3 WC1 <sub>5</sub>	***	3 W	+	5 PrCl <sub>3</sub>	-2672
2 Pr	+	WC1 <sub>6</sub>	=	M	+	2 PrCl <sub>3</sub>	-2671
5 La	+	3 MoCl <sub>5</sub>	=	3 Mo	+	5 LaCl <sub>3</sub>	-2661
3 Mg	+	C2Cl6	=	2 C	+	3 MgCl <sub>2</sub>	-2656
4 Ce	+	3 C <sub>2</sub> Cl <sub>4</sub>	-	6 C	+	4 CeCl <sub>3</sub>	<b>-</b> 2655
2 Hf	+	C <sub>2</sub> C1 <sub>6</sub>	==	2 C	+	2 HfCl3	<b>-2</b> 655
5 Nd	÷	3 WCl <sub>5</sub>	22	W E	+	5 NdCl3	<b>- 26</b> 53
2 Nd	+	WC16	==	W	+	2 Nacl <sub>3</sub>	<b>- 265 2</b>
4 La	+	3 C2C14		6 C	+	4 LaCl <sub>3</sub>	-2643
2 Sc	+	C <sub>2</sub> C1 <sub>6</sub>	==	2 C	+	2 ScCl <sub>3</sub>	-2638
4 Y	+	3 WC1 <sub>4</sub>	=	3 W	+	4 YCl <sub>3</sub>	-2632
3 Th	+	2 C <sub>2</sub> Cl <sub>6</sub>	222	4 C	+	3 ThCl <sub>4</sub>	- 26 29
5 Pr	+	3 MoCl <sub>5</sub>	===	3 Mo	+	5 PrCl <sub>3</sub>	-2617
4 Li	+	WC14	=	W	+	4 LiCl	-2612
4 Pr	+	3 C2C14	<b>22</b>	6 C	+	4 PrCl <sub>3</sub>	~2609
5 Nd	+	3 MoCl <sub>5</sub>	<b>233</b>	3 Mo	+	5 NdCl <sub>3</sub>	-2598
2 Zr	+	C2C16	<b></b>	2 C	+	2 ZrCl <sub>3</sub>	<b>~2596</b>
4 Nd	+	3 C <sub>2</sub> Cl <sub>4</sub>	<u> </u>	6 C	+	4 NdCl <sub>3</sub>	<b>~25</b> 93
5 Ba	+	2 ReCl <sub>5</sub>	==	2 Re	+	5 BaCl <sub>2</sub>	-2576
5 Y	+	3 WCl <sub>5</sub>	22	3 W	+	5 YC1 <sub>3</sub>	<b>-2</b> 558
2 Y	+	WC16	₽¥.	W	+	2 YC1 <sub>3</sub>	- 2558
5 Li	+		=	W	+	5 LiCl	-2556
6 Li	+	wc16	<b>=</b>	W	+	6 LiCl	-2556
3 Sr	+	c <sub>2</sub> cl <sub>6</sub>	201	2 C		<i>L</i> .	- 2547
2 Ca	+	WC14	=	W	+	2 CaCl <sub>2</sub>	- 25 29
4 Li	+	$c_2cl_4$	202	2 C			- 25 23
4 Ce	+	3 CC1 <sub>4</sub>	7777	3 C	+	4 CeCl <sub>3</sub>	- 25 23
Ce	+	MoCl <sub>3</sub>	123	Мо	+	1 CeCl <sub>3</sub>	25 21

Table 28 (cont.)

		Rea	actio	on			Enthalpy,
4 Y	+	3 C <sub>2</sub> Cl <sub>4</sub>	=	6 C	17	4 YC1 <sub>3</sub>	-2516
4 La	+	3 CC1 <sub>4</sub>	=	3 C	+	4 LaCl <sub>3</sub>	-2513
5 Li	+	MoCl <sub>5</sub>	=	Мо	+	5 LiCl	-2512
La	+	MoCl <sub>3</sub>	=	Mo	+	LaCl <sub>3</sub>	-2509
5 Y	+	3 MoCl <sub>5</sub>	=	3 Mo	+	5 YCl <sub>3</sub>	<b>- 2</b> 500
3 Be	+	C2Cl6	=	2 C	+	3 BeCl <sub>2</sub>	-2494
3 Ca	+	WCl <sub>6</sub>	=	W	+	3 CaCl <sub>2</sub>	- 2477
5 Ca	+	2 WC1 <sub>5</sub>	=	2 W	+	5 CaCl <sub>2</sub>	-2476
4 Pr	+	3 CC1 <sub>4</sub>	=	3 C	+	4 PrCl <sub>3</sub>	- 2476
Pr	+	MoC1 <sub>3</sub>	=	Mo	+	PrCl <sub>3</sub>	-2464
3 Ba	+	<sup>C</sup> 2 <sup>Cl</sup> 6	=	2 C	+	3 BaCl <sub>2</sub>	-2462
4 Nd	+	$3$ CCl $_4$	=	3 C	+	4 NdCl <sub>3</sub>	2459
2 Ca	+	$c_2cl_4$	=	2 C	+	2 CaCl <sub>2</sub>	-2457
Nd	+	MoCl <sub>3</sub>	=	Мо	+	NdCl3	-2444
4 U	+	3 WCl $_{f 4}$	=	3 W	+	4 UCl <sub>3</sub>	-2436
5 Ca	+	2 MoCl <sub>5</sub>	=	2 Mo	+	5 CaCl <sub>2</sub>	- 2432
4 Li	+	$CC1_4$	=	C	+	4 LiCl	-2408
2 Mg	+	$\mathtt{WCl}_4$	=	W	+	2 MgCl <sub>2</sub>	-2396
5 Ce	+	3 NbCl <sub>5</sub>	=	3 Nb	+	5 CeCl <sub>3</sub>	-2395
3 Li	+	MoCl <sub>3</sub>	=	Мо	+	3 LiCl	-2387
5 La	+	3 NbCl <sub>5</sub>	=3	3 Nb	+	5 LaCl <sub>3</sub>	-2386
5 Ce	+	3 TaCl <sub>5</sub>	-	ST &	+	5 CeCl <sub>3</sub>	-2374
4 Y	+	3 CC1 <sub>4</sub>	==	3 C	+	4 YCl <sub>3</sub>	-2371
2 U	+	WC16	==	W	+	2 UC1 <sub>3</sub>	-2369
5 บ	+	3 WCl <sub>5</sub>	=	3 W	+	5 UCl <sub>3</sub>	-2368
4 U	+	3 C <sub>2</sub> Cl <sub>4</sub>	=	6 C	+	4 UCl <sub>3</sub>	- 2368
4 Hf	+	3 WCl <sub>4</sub>	=	3 W	+	4 HfCl <sub>3</sub>	-2365
4 Sc	+	3 WCl <sub>4</sub>	=	3 W	+	4 ScCl <sub>3</sub>	- 2365
5 La	+	3 TaCl <sub>5</sub>	=	3 Ta	+	5 LaCl <sub>3</sub>	-2365
2 Sr	+	WC14	=	W	+	2 SrCl <sub>2</sub>	-2357
Ce	+	AuCl <sub>3</sub>	=	Au	+	CeCl <sub>3</sub>	-2349

Table 28 (cont.)

		Rea	ctio	on			Enthalpy, cal/cc
Th	+	WCl <sub>4</sub>	=	W	+	$\mathtt{ThCl}_4$	-2347
2 Mg	+	c <sub>2</sub> ci <sub>4</sub>	=	2 C	+	2 MgCl <sub>2</sub>	-2343
La	+	AuCl <sub>3</sub>	=	Au	+	LaCl <sub>3</sub>	-2342
5 Pr	+	3 NbCl <sub>5</sub>	=	3 Nb	+	5 PrCl <sub>3</sub>	-2341
5 Mr.	+	2 ReCl <sub>5</sub>	=	2 Re	+	5 MnCl <sub>2</sub>	<b>-2</b> 339
2 Ca	+	CCl <sub>4</sub>	=	C	+	2 CaCl <sub>2</sub>	-2339
3 Mg	+	WC16	=	W	+	3 MgCl <sub>2</sub>	-2338
Y	+	MoCl <sub>3</sub>	=	Mo	+	YC13	-2336
5 Mg	+	2 WCl <sub>5</sub>	=	2 W	+	5 MgCl <sub>2</sub>	-2336
2 Sr	+	$c_2cl_4$	=	2 C	+	2 SrCl <sub>2</sub>	- 23 24
5 No	+	$3 \text{ NbCl}_5$	=	dM E	+	5 NdCl3	23 20
5 Pr	+	3 TaCl <sub>5</sub>	=	3 Ta	+	5 PrCl <sub>3</sub>	- 23 20
4 Sc	: +	$3 C_2Cl_4$	=	6 C	+	4 ScCl <sub>3</sub>	-2318
3 Sr	+	WC16	=	W	+	3 SrCl <sub>2</sub>	-2316
4 Hf	+	$3 C_2Cl_4$	=	6 C	+	4 HfCl <sub>3</sub>	-2316
5 Sr	+	2 WC1 <sub>5</sub>	=	2 W	+	5 SrCl <sub>2</sub>	-2315
3 Ca	+	2 MoCl <sub>3</sub>	<b>=</b>	2 Mo	+	3 CaCl <sub>2</sub>	-2307
5 U	+	3 MoCl <sub>5</sub>	=	3 Mo	+	5 UCl <sub>3</sub>	-2306
4 Zr	+	$3 \text{ WCl}_4$	=	3 W	+	4 ZrCl <sub>3</sub>	-2306
2 Sc	; +	WC16	=	W	+	2 ScCl <sub>3</sub>	-2306
Pr	. +	AuCl <sub>3</sub>	=	Au	+	PrCl <sub>3</sub>	-2306
5 Sc	: +	3 WC1 <sub>5</sub>	===	3 W	+	5 ScCl <sub>3</sub>	, -2305
Tì	+	C2Cl4	=	2 C	+	$\mathtt{ThCl}_{4}^{\circ}$	-2304
	+	WC16		W	+	2 HfCl <sub>3</sub>	-2302
5 Hf	+	3 WC1 <sub>5</sub>	=	W E	+	5 HfCl <sub>3</sub>	-2301
5 No	+	3 TaCl <sub>5</sub>	=	3 Ta	+	5 NdCl <sub>3</sub>	-2298
	+	J	=	ИÞ	+		-2288
	1 +	AuCl <sub>3</sub>	=	Au	+	NdC13	-2288
3 T	7 +	2 WCl <sub>6</sub>	=	2 W		**	-2287
5 T	, +	4 WC1 <sub>5</sub>	<b>±</b>	4 W	+	5 ThCl <sub>4</sub>	-2285
2 Ba	* +	WCl <sub>4</sub>	=	W	+	2 BaCl <sub>2</sub>	-2283

Table 28 (cont.)

			Reaction	on			Enthalpy, <u>cal/cc</u>
5 Mg	+	2 MoC	:1 <sub>5</sub> =	2 Mo	+	5 MgCl <sub>2</sub>	-2282
5 Al	+	3 ReC	:15 =	3 Re	+	5 AlCl.3	-2278
5 Sr	+	2 MoC	:15 =	2 Mo	+	5 SrCl <sub>2</sub>	-2276
4 Zr	+	3 C <sub>2</sub> C	14 =	6 C	+	4 ZrCl <sub>3</sub>	-2273
5 Li	+	TaC	1 <sub>5</sub> =	Ta	+	5 LiCl	-2270
3 Li	+	AuC	:13 =	Au	+	3 LiCl	-2266
2 Ba	+	c <sub>2</sub> c	14 =	2 C	+	2 BaCl <sub>2</sub>	-2265
5 Sc	+	3 MoC	15 =	3 Мо	+	5 ScCl <sub>3</sub>	-2248
3 Ba	+	WCl	6	W	+	3 BaCl <sub>2</sub>	-2247
2 Zr	+	WCl	6	W	+	2 ZrCl <sub>3</sub>	-2247
5 Ba	+	2 WCl		2 W	+	5 BaCl <sub>2</sub>	-2246
5 Zr	+	3 WC1	5 =	3 W	+	5 ZrCl <sub>3</sub>	-2245
5 Hf	+	3 Moc	15 =	3 Mo	+	5 HfCl <sub>3</sub>	- 2240
5 Ti	+	3 Rec	15 =	3 Re	+	5 TiCl <sub>3</sub>	-2229
2 Ce	+	3 WCl	2 =	3 W	+	2 CeCl <sub>3</sub>	-2228
5 Th	+	4 Moc	:15 =	4 Mo	+	5 ThCl $_4$	-2226
2 La	+	3 WC1	2 =	3 W	+	2 LaCl <sub>3</sub>	-2223
2 Sr	+	CC1	4 =	C	+	2 SrCl <sub>2</sub>	-2213
5 Ba	+	2 MoC	~	2 Mo	+	5 BaCl <sub>2</sub>	-2210
4 U	+	3 CC1	4 =	3 C	+	4 UC1 <sub>3</sub>	-2210
5 Ca	+	2 NbC	<b>₩</b>	2 Nh	+	5 CaCl <sub>2</sub>	-2209
5 Y	+	3 NbC	15 =	3 Nb	+	5 YCl <sub>3</sub>	2208
3 Ca	+	2 Auc	13 =	2 Au	. +	3 CaCi <sub>2</sub>	-2201
2 Ce	+	3 Moc	12 =	3 Mo	+		-2200
2 Mg	+	CC1	4	С	+	2 MgCl <sub>2</sub>	-2198
Y	+	Auc		Au	. +	YC13	
2 La	+	3 Moc	:12 =	3 Mo	+	2 LaCl <sub>3</sub>	-2196
5 Ca	+	2 TaC	:15 =	2 Ta	+	5 CaCl <sub>2</sub>	-2191
3 Mn	+	c <sub>2</sub> c	16 =	2 C	+	3 MnCl <sub>2</sub>	-2188
5 Na	+	ReC	15 =	Re	+	5 NaCl	-2185
5 Zr	+	3 Moc	:1,5 =	3 Mo	+	5 ZrCl <sub>3</sub>	-2185

Table 28 (cont.)

	والمساورة والماراة		Reaction	on			Enthalpy, cal/cc
5 Y	+	3 TaC	15 =	3 Ta	+	5 YC1 <sub>3</sub>	-2184
2 Pr	+	3 MCJ		3 W	+	2 PrCl <sub>3</sub>	-2182
2 Be	+	c <sub>2</sub> c:		2 C	+	2 BeCl <sub>2</sub>	-2168
4 Sc	+	3 CC1		3 C	+	4 ScCl <sub>3</sub>	-2168
3 Sr	+	2 MoC	-	2 Mo	+	3 SrCl <sub>2</sub>	-2166
2 Be	+	WC1	4 =	W	+	2 BeCl <sub>2</sub>	-2164
2 Nd	+	3 WCl		3 W	+	2 NdCl3	-2162
2 Li	+	WC1	2	M	+	2 LiCl	-2159
2 Ba	+	CCI		C	+	2 BaCl <sub>2</sub>	-2159
4 Hf	+	3 CC1	- 4	3 C	+	4 HfCl <sub>3</sub>	-2157
2 Pr	+	3 MoC		3 Mo	+	2 PrCl <sub>3</sub>	-2153
Th	+	CCl		. С	+	ThCl <sub>4</sub>	-2148
2 Ce	+	3 CuC		3 Cu	+	2 CeCl <sub>3</sub>	-2144
2 La	+	3 CuC	1 <sub>2</sub> =	3 Cu	+	2 LaCl <sub>3</sub>	-2141
U	+	MoC:	13 =	Mo	+	UC13	-2136
2 Al	+	c <sub>2</sub> c:	1 <sub>6</sub> =	2 C	+	2 AlCl <sub>3</sub>	-2135
2 Li	+	MoC.	-	Mo	+	2 LiCl	-2134
2 Nd	+	3 MoC	1 <sub>2</sub> =	3 Mo	+	2 NdCl <sub>3</sub>	-2132
3 Mg	+	2 MoC	13 =	2 Mo	+	3 MgCl <sub>2</sub>	-2130
б Иа	+	c <sub>2</sub> c:	16 =	2 C	+	6 NaCl	-2119
4 Zr	+	3 CC1	4	3 C	+	4 ZrCl <sub>3</sub>	-2113
3 Ba	+	2 MoC	i <sub>3</sub> =	2 Mo	+	3 BaCl <sub>2</sub>	_2108
3 Be	+	WCl	5	M	+	3 BeCl <sub>2</sub>	-2106
5 Be	+	2 WC1		2 W	+	5 BeCl <sub>2</sub>	-2103
2 Pr	+	3 CuC	-	3 Cu	+	-	-2097
2 Ti	+	c <sub>2</sub> c:	-	2 C	+	•	
5 V	+	2 ReC	-	2 Re	+	~	-2092
3 Sr	+	2 AuC	-	2 Au	+	3 SrCi <sub>2</sub>	-2092
Sc	+	MoC	•	Mo	+	ScCl <sub>3</sub>	
Ca	+	WCl	-	W	+	CaCl <sub>2</sub>	
2 Li	+	CuC	-	Cu	+	2 LiCl	-2088

Table 28 (cont.)

			Reac	tion				Enthalpy, _cal/cc
5	Sr	+	2 NbCl <sub>5</sub>	=	2 Nb	+	5 SrCl <sub>2</sub>	-2082
2	Nd	+	3 CuCl <sub>2</sub>	==	3 Cu	+	2 NdCl3	-2076
	Се	+	FeCl <sub>3</sub>	=	Fe	+	CeCl <sub>3</sub>	- 2075
	La	+	FeCl <sub>3</sub>	=	Fe	+	LaCl <sub>3</sub>	-2073
	Hf	+	MoCl <sub>3</sub>	=	Мо	+	HfCl <sub>3</sub>	-2072
5	Sr	+	2 TaCl <sub>5</sub>	=	2 Ta	+	5 SrCl <sub>2</sub>	- 2065
3	Th	+	4 MoCl <sub>3</sub>	=	4 Mo	+	3 ThCl <sub>4</sub>	- 2063
	Ca	+	MoCl <sub>2</sub>	=	Мо	+	CaCl <sub>2</sub>	-2062
2	Y	+	3 WCl <sub>2</sub>	=	3 W	+	2 YC1 <sub>3</sub>	- 2056
3	Ba	+	2 AuCl <sub>3</sub>	=	2 Au	+	3 BaCl <sub>2</sub>	-2048
3	Mg	+	2 AuCl <sub>3</sub>	=	2 Au	+	3 MgCl <sub>2</sub>	-2042
	Ce	+	3 AuCl	=	3 Au	+	CeCl <sub>3</sub>	-2040
	La	+	3 AuCl	=	3 Au	+	LaCl <sub>3</sub>	- 2039
	υ	+	AuCl <sub>3</sub>	==	Au	+	UC13	<b>- 2</b> 039
5	Вe	+	2 MoCl <sub>5</sub>	=	2 Mo	+	5 BeCl <sub>2</sub>	-2037
5	Ba	+	2 NbCl <sub>5</sub>	=	2 Nb	+	5 BaCl <sub>2</sub>	-2031

Table 29

MOST ENERGETIC CHLORIDE REACTIONS WITH METALS,
IN TERMS OF GRAVIMETRIC ENTHALPY

				Reac	tion			-1-1	· · · · · · · · · · · · · · · · · · ·		Enthalpy, cal/g
	Li	+		BCl	=		В	+		LiCl	-2316
4	Li	+		C <sub>2</sub> Cl <sub>4</sub>	=	2	C	+	4	LiCl	-2002
4	Li	+		cc1 <sub>4</sub>			C	+	4	LiCl	<b>-</b> 1968
6	Li	+		c <sub>2</sub> ci <sub>6</sub>	=	2	C	+	6	LiCl	-1933
	Ca	+	2	BCl	=	2	В	+		CaCl <sub>2</sub>	-1818
	Na	+		BC1	=		В	+		NaCl	-1787
	Mg	+	2	BCl	=	2	В	+		MgCl <sub>2</sub>	-1750
	Ве	+	2	BCl	=	2	$\mathcal{B}$	+		BeCl <sub>2</sub>	-1708
	Sc	+ .	3	BCl	=	3	В	+		ScCl <sub>3</sub>	-1619
2	Ca	+		C2Cl4	=	2	C	+	2	CaCl <sub>2</sub>	-1532
	K	+		BC1	=		В	+		KC1	-1519
4	Na	+		C2Cl4	=	2	C	+	4	NaCl	-1512
2	Ca	+		CC14	=		С	+	2	CaCl <sub>2</sub>	-1481
	Al	+	3	BCl	=	3	В	+		AlCl <sub>3</sub>	-1465
4	Na	+		CCl <sub>4</sub>	=		C	+	4	NaCl	-1463
3	Ca	+		C2CI6	=	2	C	+	. 3	CaCl <sub>2</sub>	-1462
6	Na	+		C2C16	=	2	C	+	6	NaCl	-1444
6	Li	+		MoCl <sub>6</sub>	=		Mo	+	6	LiCl	-1416
2	Mg	+		C2Cl4	=	2	C	+	2	MgCl <sub>2</sub>	-1416
3	Li	+		BC13	-		В	+	3	LiCl	-1399
	Sr	+	2	BC1	=	2	В	+		SrCl <sub>2</sub>	-1382
	Y	+	3	BCl	=	3	В	+	. •	YC13	-1368
2	Mg	+		CC1 <sub>4</sub>	=		C	+	2	MgCl <sub>2</sub>	-1350
	Li	+		AlCl		,				LiC1	-1337
3	Mg	+		C2Cl6	=	2	C	+	3	MgCl <sub>2</sub>	-1330
2	Ве			C2C14	=	2	C	+		BeCl <sub>2</sub>	-1313
4	Li	+		CrCl <sub>4</sub>			Cr		4	LiCl	-1294
	Ti	+	3	BCl	=	3	B	+		TiCl <sub>3</sub>	-1294
5	Li	+		MoCl <sub>5</sub>	=		Мо	+	5	LiCI	-1291

Table 29 (cont.)

				Reactio	on						Enthalpy,
4	Sc	+	3	C2Cl4	=	6	С	+	4	ScCl <sub>3</sub>	-1290
4	K	+		C <sub>2</sub> Cl <sub>4</sub>	=	2	C	+	4	KC1	-1283
4	Li	+		MnCl <sub>4</sub>	=		Mn	+	4	LiCl	-1250
	Zr	+	3	BCl	≈	3	В	+		ZrCl <sub>3</sub>	-1237
4	K	+		CCl <sub>4</sub>	=;		C	+	4	KCl	-1235
2	Вe	+		CCl <sub>4</sub>	≈.		С	+	2	BeCl <sub>2</sub>	-1229
	La	4.	3	BCl	=	3	В	+		LaCl <sub>3</sub>	-1225
5	Li	+		NbCl <sub>5</sub>	=		Nb	+	5	LiCl	-1224
6	K	+		C2Cl6	=	2	C	+	6	KC1	-1224
4	Sc	+	3	$CCl_4$	=	3	C	+	4	ScCl <sub>3</sub>	-1221
3	Вe	+		<sup>C</sup> 2 <sup>Cl</sup> 6	=	2	C	+	3	BeCl <sub>2</sub>	-1208
	Ce	+	3	BCl	=	3	В	+		CeCl <sub>3</sub>	-1208
2	Sc	+		<sup>C</sup> 2 <sup>Cl</sup> 6	=	2	C	+	2	ScCl <sub>3</sub>	-1204
4	Li	+		$\operatorname{SiCl}_4$	=		Si	+	4	LiCl	-1203
	Si	+	4	BC1	=	4	В	+		sicl <sub>4</sub>	-1197
	Pr	+	3	BCl	=	3	В	+		PrCl <sub>3</sub>	-1196
4	Li	+		MoCl <sub>4</sub>	=		Mo	+	4	LiCl	-1174
	Nd	+	3	BCl	==	3	В	+		NdCl3	-1169
2	Sr	+		C <sub>2</sub> Cl <sub>4</sub>	=	2	С	+	2	SrCl <sub>2</sub>	-1152
5	Li	+		Sb Cl <sub>5</sub>	=		Sb	+		LiCl	-1149
4	Li	+		VCl <sub>4</sub>	=		V	+	4	LiCl	-1146
	Li	+		GeCl	=		Ge	+		LiCl	-1131
	Mn	+	2	BC1	==	2	В	+		MnCl <sub>2</sub>	-1128
	V	+	3	BCl	=	3	В	+		vcr <sup>3</sup>	-1126
3	Ca			MoCl <sub>6</sub>			Мо	+	3	CaCl <sub>2</sub>	-1119
6	Na	+		MoCl <sub>6</sub>	=		140	+	6	NaCl	-1118
	Ba	+	2	BCl	=	2	В	+		BaCl <sub>2</sub>	-1116
6	Li	+		WC16	==		W	+	Ó	LiCl	-1112
	Cr	+	3	BCl	=	3	В	+		CrCl <sub>3</sub>	-1107
2	Sr	+		CCl <sub>4</sub>			С	+		SrCl <sub>2</sub>	-1102
3	Sr	+		c₂cl <sub>ô</sub>	=	2	С	+	3	SrCl <sub>2</sub>	-1092

Table 29 (cont.)

<del></del>		F	Reacti	on		*******************************			Enthalpy, cal/g
Ca	+	2 1	rici	=	2	Al	+	CaCl <sub>2</sub>	-1092
Na	+	I	Alcl	=		Al	+	NaCl	-1092
4 Y	+	3 (	2 <sub>2</sub> C1 <sub>4</sub>	=	6	C	+	4 YCl <sub>3</sub>	-1090
4 Al	+	3 (	22014	=	6	C	+	4 AlCl <sub>3</sub>	-1083
4 Li	+	C	GeCl <sub>4</sub>	=		Ge	+	4 LiCl	-1076
3 Li	+	F	reCl <sub>3</sub>	=		Fe	+	3 LiCl	-1072
5 Li	+	I	ReCl <sub>5</sub>	=		Re	+	5 LiCl	-1050
3 Na	+	I	3C1 <sub>3</sub>	=		В	+	3 NaCl	-1045
3 Ca	+		3C1 <sub>3</sub>	=	2	В	+	3 CaCl <sub>2</sub>	-1043
5 Na	+		loC1 <sub>5</sub>	=		Mo	+	5 NaCl	-1031
5 Ca	+	2 1	40Cl <sub>5</sub>	=	2	Mo	+	5 CaCl <sub>2</sub>	-1028
4 Y	+	3 (	CC1 <sub>4</sub>	=	3	C	+	4 YCl <sub>3</sub>	-1027
3 Li	+		ioCl <sub>3</sub>	=		Мо	+	3 LiCl	-1022
5 Li	+		VC1 <sub>5</sub>	=		W	+	5 LiCl	-1021
2 Y	+		22C1 <sub>6</sub>	=	2	Ç	+	2 YC1 <sub>3</sub>	-1016
4 Na	+		CrCl <sub>A</sub>	=		Çr	+	4 NaCl	-1010
2 Ca	+	C	CrCl <sub>4</sub>	=		Cr	+	2 CaCl 2	-1007
3 Li	+		unCl <sub>3</sub>	=		Mn	+	3 LiCl	-1005
Na	+	(	GeCl	=		Ge	+	NaCl	<b>-</b> 997
Ca	+	2 (	GeC1	=	2	Ge	+	CaCl <sub>2</sub>	- 994
4 La	+	3 (	C <sub>2</sub> Cl <sub>4</sub>	=	6	C	+	4 LaCl3	- 992
4 Al	+		CC14	=	3	С	+	4 AlCl3	• - 992
2 Li	+		CuCl <sub>2</sub>	==		Cu	+	2 LiCl	- 985
6 K	+		MoCl <sub>6</sub>	=		Мо	+	6 KCl	- 984
Hf	+		_	=	4	В	+	$HfCl_{4}$	- 982
4 Na	+	1	MnCl <sub>4</sub>	23		Mn	+	*	- 979
2 A1	+		C <sub>2</sub> C1 <sub>6</sub>		2	Ç	+	2 AlCl <sub>3</sub>	- 978
ĸ	+		Alcı			Al	+	KC1	- 977
5 Na	+	ı	NbCl <sub>5</sub>	=		Nb	+	5 NaCl	- 976
4 Ce	+		C <sub>2</sub> Cl <sub>4</sub>		6	С	+	4 CeCl <sub>3</sub>	- 975
Rb	+		BC1	+		В	+	RbC1	- 975

Table 29 (cont.)

				<del></del>			
		Reacti	on				Enthalpy, cal/q
2 Ca	+	$MnCl_4$	=	Mn	+	2 CaCl <sub>2</sub>	- 974
4 Li	+	TiCl4	=	Ti	+	4 LiCl	- 972
5 Ca	+	2 NbCl <sub>5</sub>	=	2 Nb	+	5 CaCl 2	- 971
3 Mg	+	MoCl <sub>6</sub>	12	Mo	+	3 MgCl <sub>2</sub>	- 969
Ga	+	3 BCl	=	3 B	+	GaCl <sub>3</sub>	- 969
4 Pr	+	$3 c_2 c_4$	=	6 C	+	4 PrCl <sub>3</sub>	- 963
Mg	+	2 AlCl	=	2 Al	+	MgCl <sub>2</sub>	- 962
4 Zr	+	$3 c_2 cl_4$	<b>#</b> .	5 C	+	4 ZrCl <sub>3</sub>	- 954
Zn	+	2 BCl	=	2 B	+	ZnCl <sub>2</sub>	- 953
4 Na	+	${ t MoCl}_4$	=	Мо	+	4 NaCl	- 952
Li	+	GaCl	=	Ga	+	LiCl	- 951
2 Ca	+	$MoCl_4$	=	Мо	+	2 CaCl <sub>2</sub>	- 946
4 Ti	+	$3 C_2C1_4$	=	6 C	+	4 TiCl <sub>3</sub>	- 944
4 La	+	$3$ CCl $_{f 4}$	=	3 C	+	4 LaCl <sub>3</sub>	- 938
4 Nd	+	$3 C_2C1_4$	=	6 C	+	4 NdCl <sub>3</sub>	- 938
5 Li	+	TaCl <sub>5</sub>	=	Ta	+	5 LiCl	- 937
5 Na	+	sbc15	=	. Sb	+	5 NaCl	- 933
2 La	+	c2cl6	=	2 C	+	2 LaCl <sub>3</sub>	- 931
4 Li	+	$ReCl_4$	=	Re	+	4 LiCl	- 929
Th	+	4 BCl	<b>=</b>	4 B	+	ThCl <sub>4</sub>	- 928
K	+	GeCl	=	Ge	÷	KCl	- 928
5 Ca	+	2 SbCl <sub>5</sub>	ᇣ	2 Sb	+	5 CaCl <sub>2</sub>	- 927
2 Ba	+	C2Cl4	2	2 C	+	2 BaCl 2	- 926
4 Ce	+	3 CC1 <sub>4</sub>	23	3 C	+	4 CeCl <sub>3</sub>	- 921
6 Na	+	wc1 <sub>6</sub>	=	M	+	6 NaCl	- 917
5 K	+	MoCl <sub>5</sub>	=	Mo	+	5 KCl	- 917
6 Li	+	Al <sub>2</sub> Cl <sub>6</sub>		2 Al	+	6 LiCl	- 916
4 Na	+	SiCl <sub>4</sub>	=		+		~ 916
2 Ce	+	C <sub>2</sub> Cl <sub>6</sub>	=	2 C	+	2 CeCl <sub>3</sub>	- 914
3 Ca	+	WC1 <sub>6</sub>	=	W	+	$3 \text{ CaCl}_2$	- 911

Table 29 (cont.)

				Rea	ctio	on						nalpy,
4	Pr	+	3	CC1 <sub>4</sub>	=	3	C	+	4 Pr	Cl <sub>3</sub>	-	908
4	Li	+		OsCl <sub>4</sub>	=		0s	+	4 Li	_	_	908
	Mg	+	2	GeCl	=	2	Ge	+	Mg	Cl <sub>2</sub>	****	907
2	Ca	+		SiCl <sub>4</sub>	=		Si	+	2 Ca	Cl <sub>2</sub>	-	907
3	K	+		BCl <sub>3</sub>	=		В	+	3 KC	:1	-	906
4	Li	+		WCl4	<b>a</b>		M	+	4 Li	.Cl	_	904
4	Li	+		SnCl <sub>4</sub>	=		Sn	+	4 Li	.Cl	-	903
	Ge	+	4	BCl	=	4	В	+	Ge	Cl <sub>4</sub>	-	901
2	Pr	+		C2C16	= .	2	C	+	2 Pr	C13	_	901
4	Na	+		VC14	=		V	+	4 Na	C1	_	895
	Fe	+	2	BC1	=	2	В	+	Fe	Cl <sub>2</sub>	_	894
Ϋ́	K	+		CrCl <sub>4</sub>	=		Cr	+	4 KC	:1	-	892
	Sc	+	3	AlC1	30	3	Al	+	Sc	:C1 <sub>3</sub>	-	887
2	Ca	+		VCl <sub>4</sub>	=		V	+	2 Ca	Cl <sub>2</sub>	-	886
4	Zr	+	3	CCl <sub>4</sub>	=	3	Ç	+	4 Zr	C13	-	885
	Sr	+	2	AlCl	<b>63</b>	2	Al	+	Sr	cl <sub>2</sub>		885
3	Li	+		CrCl <sub>3</sub>	=		Cr	+	3 Li	.Cl	-	884
4	Nd	+	3	CCl <sub>4</sub>	=	3	С	+	4 Nd	C13	-	883
2	Sc	+		MoC16	=		Мо	*	2 Sc	:C1 <sub>3</sub>	-	882
3	Sr	+		MoC1 <sub>6</sub>	=		Мо	+	3 Sr	cl <sub>2</sub>	-	881
2	Ва	+		CC1 <sub>4</sub>	=		C	+	2 Ba	Cl <sub>2</sub>	-	881
5	Na	+		ReCl <sub>5</sub>	=		Re	+	5 Na		• -	088
2	Zr	+		C2C16	=	2	С	+	2 Zr	cı,	-	877
2	Nd	+		C2C16	=	2	С	+	2 Nd		-	876
3	Ba	+		C2C16	=	2	C	+	3 Ba	Kl <sub>2</sub>	-	876
5	Mg	+	2	MoCl <sub>5</sub>	ໝ	2	Mo	+	<b>5</b> Mg	Cl <sub>2</sub>	•	£76
3	I.i	+		vc1 <sub>3</sub>	=		V	+	3 Li	Cl	*	976
5	Ca	+		ReC1 <sub>5</sub>		2	Re	÷	5 Ca	Cl <sub>2</sub>	-	873
5	K	+		NbCl <sub>5</sub>	=		Ир	+	5 KC	21	-	871
4	K	۵.		MnCl <sub>4</sub>	222		Mn	+	4 KC	21	-	868

Table 29 (cont.)

	· · ·			Rea	ctio	on						nalpy, al/g
	Sr	+	2	GeCl	<b>≂</b>	2	Ge	+		SrCl <sub>2</sub>	-	865
	Sc	+	3	GeCl	=	3	Ge	+		ScCl <sub>3</sub>	-	861
4	Na	+		GeCl <sub>4</sub>	=		Ge	+	4	NaCl	-	853
4	Тi	+	3	CCl <sub>4</sub>	=	3	C	+	4	TiCl <sub>3</sub>		357
4	K	+		MoCl <sub>4</sub>	=		Мо	+	4	KCl	_	006
3	Na	+		FeCl <sub>3</sub>	=		Fe	+	3	NaCl ·	-	355
5	Na	+		WC1 <sub>5</sub>	=		W	+	5	NaCl		855
3	Li	+		GaCl <sub>3</sub>	=		Ga	+	3	LiCl	-	851
	Ço	+	2	BC1	=	2	В	+		CoCl <sub>2</sub>	-	851
2	Ca	+		GeCl <sub>4</sub>	=		Ge	+	2	CaCl <sub>2</sub>	-	848
2	Ti	+		C <sub>2</sub> Cl <sub>6</sub>	=	2	C	+	2	TiCl <sub>3</sub>	-	847
5	Ca	+	2	W Cl <sub>5</sub>	=	2	W	+	3	CaCl <sub>2</sub>		847
3	Na	÷		MoCl3	<b>=</b>		Мо	+	3	NaCl	-	846
3	Mg	+	2	BC13	=	2	В	+	3	MgCl <sub>2</sub>	-	846
3	Ca	+	2	FeCl <sub>3</sub>	=	2	Fe	+	3	CaCl <sub>2</sub>	•••	846
5	К	+		SbCl <sub>5</sub>	=		Sb	+	5	KC1	-	841
	Ве	+	2	AlCl	=	2	Al	+		BeCl <sub>2</sub>	-	840
3	Ca	+	2	MoCl <sub>3</sub>	=	2	oM	+	3	CaCl <sub>2</sub>	-	838
2	Li	+		MoCl <sub>2</sub>	=		Мо	+	2	LiCl	***	837
	Nı	+	2	BCl	=	2	В	+		NiCl <sub>2</sub>		837
	Na	+		GaCl	=		Ga	+		NaCl	•	836
2	Mg	+		$\mathtt{CrCl}_4$	=		Cr	+	2	$MgCl_2$	` -	836
2	Li	+		NiCl <sub>2</sub>	=		Ni	+	2	LiCl		835
	U	+	4	BCl	=	4	В	+		UCl <sub>4</sub>	•••	835
6	K	+		WCl <sub>6</sub>	=		W	+	6	KCl	-	833
	Ве	+	2	GeCl	=	2	Ge	+		BeCl <sub>2</sub>	***	331
	Ca	+	2	GaCl	=	2.	Ga	+		CaCl <sub>2</sub>		830
2	Mn	+		$C_2Cl_4$	=	2	C	+	2	MnCl <sub>2</sub>	-	8 25
3	Ве	+		MoCl <sub>6</sub>	==		CM	+	3	BeCl <sub>2</sub>	_	824
		+		AlCl <sub>3</sub>				+		LiCl		823

Table 29 (cont.)

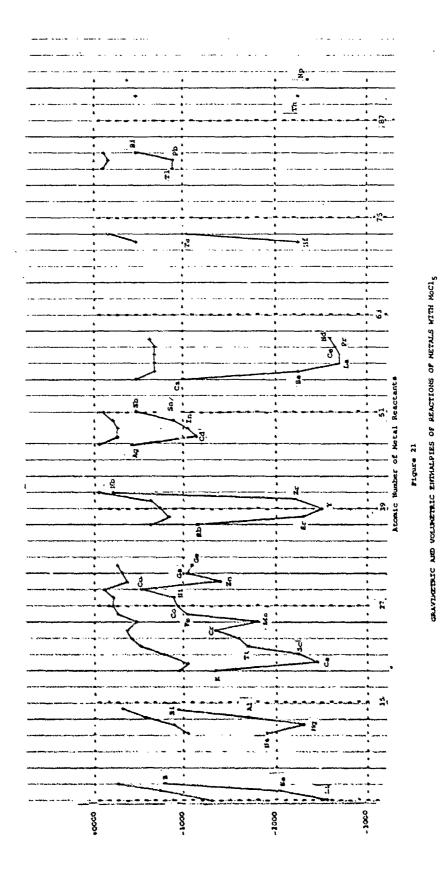
		·		Rea	ctio	n_						halpy,
5	Sr	+	2	MoCl <sub>5</sub>	=	2	Мо	+	5	SrCl <sub>2</sub>	-	821
2	Li	+		CoCl <sub>2</sub>	=		Co	+	2	LiCl	-	818
3	Li	+		AuCl <sub>3</sub>	=		Au	+	3	LiCl	_	816
2	Na	+		CuCl <sub>2</sub>	=		Cu	+	2	NaCl	-	816
5	Mg	+	2	NbCl <sub>5</sub>	=	2	Nb	+	5	MgCl <sub>2</sub>	_	811
3	Li	+		SbCl <sub>3</sub>	=		Sb	+	3	LiCl	-	810
2	Li	7		FeCl <sub>2</sub>	=		Fe	+	2	LiCl		809
	In	+	3	BCl	=	3	В	+		InCl <sub>3</sub>	_	808
4	K	+		SiCl <sub>4</sub>	=		Si	+	4	KCl	_	808
	Ca	+		CuCl <sub>2</sub>	=		Cu	+		CaCl <sub>2</sub>	_	806
5	K	+		ReCl <sub>5</sub>	=		Re	+	5	KCl		806
4	Rb	+		C2C14	==	2	С	+	4	RbCl		804
	Y	+	3	GeCl	=	3	Ge	·;•		YCl <sub>3</sub>	-	804
3	Na	+		MnCl <sub>3</sub>	=		Mn	+	3	NaCl		802
2	Mg	+		MnCl <sub>4</sub>	<b>=</b>		Mn	+	2	MgCl <sub>2</sub>	-	٤01

(tetrachloroethylene, carbon tetrachloride, and hexachloroethane), chromium tetrachloride, molybdenum hexachloride, and molybdenum pentachloride.

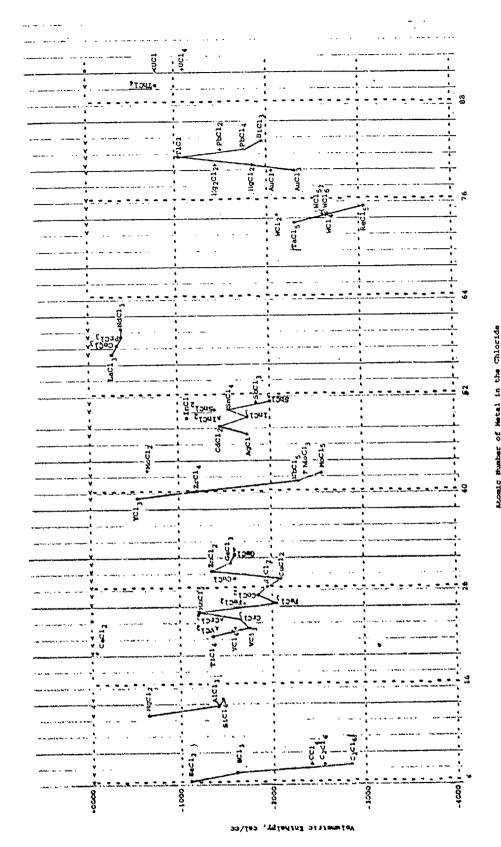
The periodic relationships of the chloride reactions are shown in Figures 21, 22, and 23. It is interesting to compare the general periodic trends, shown by the solid connecting lines, in the chloride, oxide, and fluoride systems. Lithium, which is one of the best reducing agents in the chloride systems, is of moderate efficacy in the oxide and fluoride systems. It occurs at one of the most energetic peaks in the chloride systems. Unlike the oxide systems, magnesium is more energetic than aluminum in the fluoride and chloride systems. Titanium is relatively less energetic in the chloride systems than in the fluoride and oxide systems. The areas including strontium, yttrium, zirconium, the rare earths, hafnium, and tantalum are similar in all three systems.

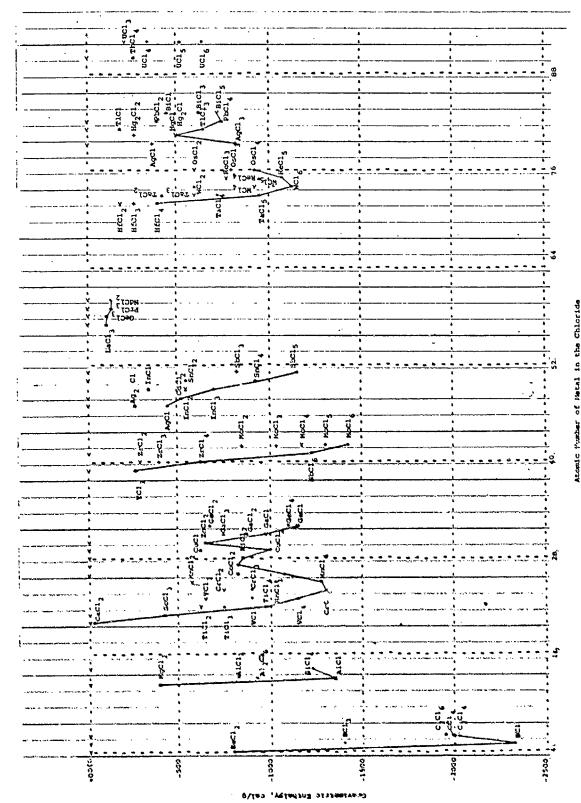
It is also of interest to compare the trends within the different periodic groups. The trends within each group are similar in all three systems except for the alkaline earths. Thus, most of the groups exhibit less energetic reactions as the atomic number increases. The primary exception to this is the titanium-zirconium-hafnium group, which exhibits an increase in the volumetric energy with increasing atomic number because the lanthanide contraction minimizes the effect of the volume. The behavior of the alkaline earths is therefore striking. Instead of decreasing in energy with increasing atomic number, maximum energy is reached at calcium. This occurs because the heat of formation of the chlorides increases monotonically at a rate which is compensated by the increase in atomic volume and weight when calcium is reached. After calcium, the increase in heat of formation is not enough to overcome the effect of the increase in atomic volume and weight.

The reactions of the chlorides with lithium metal are depicted in Figures 22 and 23. These curves are approximately the inverse of the curves in Figure 21 because the metals that are effective reducing agents form chlorides that are poor oxidizing agents. The chlorides of carbon (hexachloroethane, terrachloroethylene and carbon tetrachloride), the transition metal chlorides (vanadium trichloride, chromium trichloride, iron trichloride, cobalt dichloride, nickel dichloride, copper dichloride, molybdenum pentachloride, molybdenum trichloride tantalum pentachloride tungsten tetrachloride tungsten pentachloride and tungsten hexachloride), gold trichloride, mercury dichloride, lead tetrachloride, and bismuth trichloride are effective oxidizers on a volumetric basis. In general, the higher the oxidation state of the metal in the chloride, the more energetic are its reactions. For instance, note the volumetric outputs of molybdenum di-, tri-, and pentachloride. There are many exceptions however, such as vanadium tetra- and trichloride and tungsten tetra- and pentachloride.



Enchaty, (\*) or 'cc, (\*) cal/g





The behavior of the chlorides on a gravimetric basis is similar to the volumetric behavior. The chlorides of carbon and the chlorides of many of the transition metals are effective oxidizers. Again, the higher the oxidation state of the metal in the chloride, the more energetic are its reactions. is illustrated dramatically in Figure 23 by the chlorides of titanium, chromium, manganese, zirconium, molybdenum, indium, tin, antimony, hafnium, tantalum, tungsten, rhenium, osmium, lead, bismuth, and uranium. There are a few exceptions, such as the chlorides of boron, aluminum, gallium, germanium, and mercury. It is interesting that the first three are the first elements in Group IIIA. Evidently, in this group the addition of chloride atoms does not increase the heat of formation of the chloride enough to compensate for the increase in weight of the additional chlorine atoms. Similar charts for the other chlorides and metals indicate similar trends, except for displacement of the vertical scale.

Summaries of the volumetric and gravimetric enthalpies of all the chloride reactions are presented in Tables 30 and 31, respectively. The most energetic reactions are in the upper left-hand corner of the chart. The same trends noted previously are apparent.

Table 30 VOLUMETRIC ENTRANPIES OF REACTIONS OF METALS WITH CHLORIDES (In descending order from top to bottom and left to right)

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## J. Chromate Reactions

The reactions between 49 metals and 5 chromates were programmed on the computer. A total of 2920 possible reactions was examined, and 114 of these were printed. As mentioned previously, when two reactants undergo more than one reaction, only the most energetic one is printed. The reactions with positive enthalpies are also discarded. The chromates are the least energetic of the oxide systems examined. The most energetic reaction exhibits an enthalpy of only -3845 cal/cc.

Representative computer data for a few of the chromate reactions are illustrated in Table 32. The relatively low energies of these reactions are due primarily to the high heat of formation of the chromates. The high heats of formation of the product oxides partially compensate for this.

The periodic variation of the enthalpies of the reactions of the metals with lead chromate is shown in Figure 24. The trends are the same as those observed in the other oxide systems. The Group II metals (beryllium, magnesium, and calcium), the Group IVB metals (titanium, zirconium, and hafnium) and the rare earths (lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbiúm, holmíum, erbium, thorium, uranium, and neptunium) are effective reducing agents. With the exception of Group IVB, which is anomalous because of the lanthanide contraction, the energies within a group tend to decrease with increasing atomic number. This is apparent in Group IA (lithium, rubidium, and cesium), Group IIA (beryllium, magnesium, strontium, and barium), Group VB (vanadium, niobium, and tantalum), and Group VIB (chromium, nolybdenum, and tungsten). Except for displacement of the vertical scale, the other chromates exhibit similar trends.

The most energetic chromate reactions are listed in Tables 33 and 34. A summary of the enthalpies of all the chromate reactions is presented in Tables 35 and 36. The trends described previously are evident in Tables 35 and 36. Lead and silver chromate are the most effective oxidizers on a volumetric basis, and sodium and lead chromate are the most effective on a gravimetric basis.

Table 32

DATA ON REACTIONS OF VARIOUS METALS WITH CHROMATES

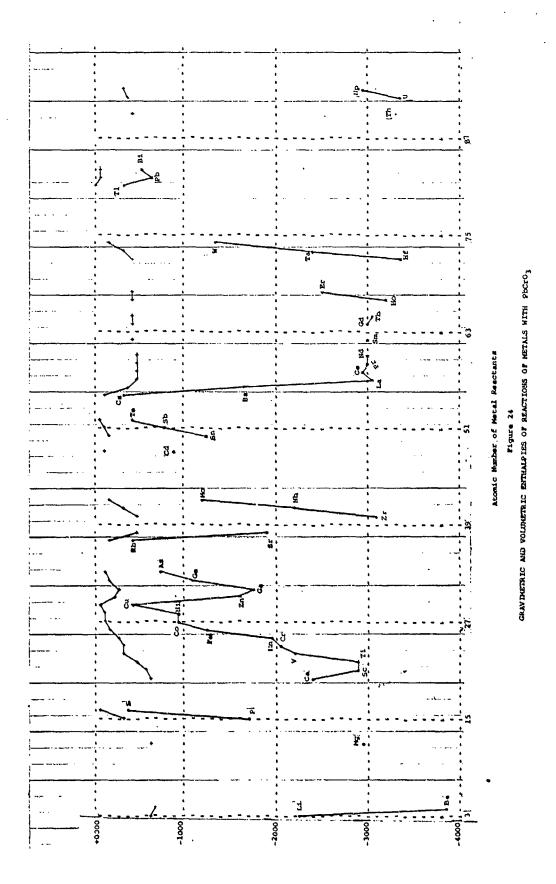
en en la la la la manage de la	3 Ge +	4 Ag <sub>2</sub> CrO <sub>4</sub>	$= 4 \text{ Ag}_2^0$	+ 3 GeO <sub>2</sub> +	2 Cr <sub>2</sub> 0 <sub>3</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	72.60 5.35 960.00 2700.00 -272.92 5.58 -176.66	-170 15 331,70 5,63	-7.31 231.76 7.14 300.00	-128.30 104,60 4.70 1000,00	-269.70 152.02 5.21 2265.00
	3 H£ +	4 Ag2CrO4	$= 4 \text{ Ag}_2^0$	+ 3 HfO <sub>2</sub> +	- 2 Cr <sub>2</sub> 0 <sub>3</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	178.50 13.30 2227.00 3200.00 -702.52 -377.18	-170°15 331.77 5.63	-7.31 231.76 7.14 300.00	-271.50 210.60 9.68 2810.00	-269.70 152.02 5.21 2265.00
	2 Ho +	2 Ag2CrO4	$= 2 \text{ Ag}_2^0$	+ Ho <sub>2</sub> 0 <sub>3</sub>	$+ cr_2^{0_3}$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/c	164.94 8.76 -393.61 6.38 -396.22 -2529.31	-170.15 331.77 5.63	-7.31 231.76 7.14 300.00	377.88	-269.70 152.02 5.21 2265.00

. Table 32 (cont.)

	2 La +	$2 \text{ Ag}_2\text{CrO}_4$	$= 2 \text{ Ag}_2^0$	+ La <sub>2</sub> 0 <sub>3</sub> +	$cr_2^{0_3}$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	138.92 6.15 880.00 1800.00 -402.01 5.77 -427.05	-170.15 331.77 5.63	-7.31 231.76 7.14 360.00	-458.00 325.84 6.51 2315.00 4200.00	-269.70 152.02 5.21 2265.00
	6 Li +	2 Ag2CrO4	$= 2 \text{ Ag}_2^0$	+ 3 Li <sub>2</sub> 0 +	$cr_2^{0_3}$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	6.94 .53 .180.00 1326.00 -371.21 3.60 -526.41	-170.15 331.77 5.63	-7.31 231.76 7.14 300.00	-142.40 29.88 2.01 1700.00	-269.70 152.02 5.21 2265.00
	.3 Mg	∴ 2 Ag <sub>2</sub> CrO <sub>4</sub>	$= 2 \text{ Ag}_2^0$	+ 3 MgO +	$cr_2^{0_3}$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants; density Gravimetric enthalpy, cal/g	24.32 1.74 650.00 1120.00 -375.53 4.61 -509.89	-170.15 331.77 5.63	-7.31 231.76 7.14 300.00	-143 84 40 32 3 58 2800 00	-269,70 152,02 5,21 2265,00

Table 32 (cont.)

	8 La +	6 PbCrO <sub>4</sub>	$= 3 \text{ Pb}_2^0$	+ 4 La <sub>2</sub> 0 <sub>3</sub> +	3 Cr <sub>2</sub> 0 <sub>3</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	138.92 6.15 880.00 1800.00 -1488.50 6.24 -487.92	-217,70 323,22 6,30 844,00	-51.20 430.42 8.34	258 225 600 115	0 2 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
	8 Li +	2 Pbcro4	= Pb <sub>2</sub> 0	+ 4 Li <sub>2</sub> 0 +	$cr_2^{0_3}$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	6.94 .53 .180.00 1326.00 -455.10 -455.10	-217.70 323.22 6.30 844.00	-51.20 430.42 8.34	-142.40 29.88 2.01 1700.00	-269.70 152.02 5.21 2265.00
	4 Mg +	+ 2 Pbcr0 <sub>4</sub>	= Pb <sub>2</sub> 0	+ 4 MgO	$+ cr_2^{0_3}$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	24.32 1.74 650.00 1120.00 -460.86 4.69 -619.67	-217.70 323.22 6.30 844.00	-51.20 430.42 8.34	-143.84 40.32 3.58 2800.00	-269.70 152.02 5.21 2265.00



Enthelpy, (\*)oel/cc, (+)cel/g

Table 33

MOST ENERGETIC CHROMATE AND DICHROMATE REACTIONS WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

					eac.	tic	on							Enthalpy, cal/cc
4	Ве	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	4	BeO	+		Cr <sub>2</sub> O <sub>3</sub>	-3845
2	U	+	2	Pb(CrO <sub>4</sub> )	=		Pb20	+	2	UO 2	+		Cr <sub>2</sub> O <sub>3</sub>	-3322
2	Hf	+	2	Pb(CrO <sub>4</sub> )	=		-			HfO <sub>2</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-3310
2	Th	+	2	Pb(CrO <sub>4</sub> )	=		Pb20	+	2	ThO <sub>2</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-3 259
8	Но	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb20	+	4	Ho 203	+	4	Ho 2 <sup>O</sup> 3	-3173
2	Zr	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	2	zro <sub>2</sub>	+		Cr <sub>2</sub> C <sub>3</sub>	-3065
8	Tb	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Tb203	+	3	Cr <sub>2</sub> 0 <sub>3</sub>	-3048
8	La	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	La 203	+	3	Cr <sub>2</sub> O <sub>3</sub>	-3046
8	$\operatorname{Sm}$	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	$Sm_2O_3$	+	3	Cr <sub>2</sub> O <sub>3</sub>	-2999
8	Nd	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	$Nd_2O_3$	+	3	Cr <sub>2</sub> O <sub>3</sub>	-2998
8	Gd	+	6	Pb(CrO <sub>4</sub> )	=	3	$Pb_2O$	+	4	Gd 203	+	3	Cr <sub>2</sub> 0 <sub>3</sub>	-2986
8	Pr	+	6	Pb(CrO <sub>4</sub> )	=	3	$^{\rm Pb}2^{\rm O}$	+	4	Pr <sub>2</sub> O <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	- 2980
8	Сe	+	6	Pb(CrO <sub>4</sub> )	=	3	$pb_2O$	+	4	$Ce_2O_3$	+	3	Cr <sub>2</sub> O <sub>3</sub>	-2939
2	Νр	+	2	Pb(CrO <sub>4</sub> )	=		$Pb_2O$	+	2	NpO <sub>2</sub>	÷		Cr <sub>2</sub> O <sub>3</sub>	-2914
4	Mg	+	2	Pb(CrO <sub>4</sub> )	=		$Pb_2O$	+	4	MgO	+		cr <sub>2</sub> 0 <sub>3</sub>	- 2907
3	Вe	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+	3	BeO	+		Cr <sub>2</sub> O <sub>3</sub>	- 2881
8	Sc	+	6	Pb'CrO <sub>4</sub> )	**	3	$Pb_2O$	+	4	Sc 203	+	3	Cr <sub>2</sub> O <sub>3</sub>	- 2879
8	Ti	+	6	Pb(CrO <sub>4</sub> )	=	3	$Pb_2O$	+	4	Ti 203	+	3	Cr <sub>2</sub> O <sub>3</sub>	-2861
3	Th	+	4	$Ag_2(CrO_4)$	==	4	Ag <sub>2</sub> 0	+	3	ThO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-2563
3	U	+	4	$Ag_2(CrO_4)$	=	4	Ag <sub>2</sub> 0	+	3	υ0 <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-2546
3	Hf	+	4	$Ag_2(CrO_4)$	==		-			HfO <sub>2</sub>			Cr <sub>2</sub> O <sub>3</sub>	-2543
2	Но	+		$Ag_2(CrO_4)$	==	2	Ag 20	+		$^{\text{Ho}}2^{\text{O}}3$	+		Cr <sub>2</sub> O <sub>3</sub>	- 25 29
8	Er	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Er <sub>2</sub> O <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	- 2499
2	La			$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+		La <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	- 2464
2	Tb	+		Ag <sub>2</sub> (CrO <sub>4</sub> )									Cr <sub>2</sub> O <sub>3</sub>	-2439
2	Nd	+	2	$Ag_2(CrO_4)$	=	2	$^{\mathrm{Ag}}2^{\mathrm{O}}$	+		$^{\text{Nd}}2^{\text{O}}3$	+		Cr <sub>2</sub> O <sub>3</sub>	-2415
	Pr			$Ag_2(CrO_4)$			_						Cr <sub>2</sub> O <sub>3</sub>	-2408
	Sm			Ag <sub>2</sub> (CrO <sub>4</sub> )			$^{\mathrm{Ag}}2^{\mathrm{O}}$	+		$\rm Sm_2O_3$	+		Cr <sub>2</sub> O <sub>3</sub>	- 2406
2	Gđ	+	2	Ag <sub>2</sub> (CrO <sub>4</sub> )	=	2	Ag <sub>2</sub> 0	+		Gd 203	+		Cr <sub>2</sub> O <sub>3</sub>	- 2398

Table 33 (cont.)

_							<b>Re</b> ac	:t:	i.oı	1				Enthalpy, cal/cc
4	Ca	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	4	CaO	+		Cr <sub>2</sub> O <sub>3</sub>	-2393
3	Zr	+	4	Ag <sub>2</sub> (CrO <sub>4</sub> )	=	4	Ag <sub>2</sub> 0	+	3	ZrO2	+	2	Cr <sub>2</sub> O <sub>3</sub>	-2377
8	Ta	+	10	Pb(CrO <sub>4</sub> )	=	5	Pb20	+	4	Ta 205	+	5	Cr <sub>2</sub> O <sub>3</sub>	-2377
2	Ce	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+		Ce <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-2371
3	Mg	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+	3	MgO	+		Cr <sub>2</sub> O <sub>3</sub>	-2348
2	Sc	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+		Sc 203	+		Cr <sub>2</sub> O <sub>3</sub>	-2306
3	Ве	+	2	Ba(CrO <sub>4</sub> )	=	2	BaO	+	3	BeO	+		Cr <sub>2</sub> 0 <sub>3</sub>	-2293
3	Иp	+	4	$Ag_2(CrO_4)$	=	4	Ag <sub>2</sub> 0	+	3	NpO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-2265
2	Ti	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+		Ti <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-2233
8	Li	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> 0	+	4	Li <sub>2</sub> 0	+		Cr <sub>2</sub> O <sub>3</sub>	-2203
2	ИÞ	+		Pb(CrO <sub>4</sub> )	=		$Pb_2^0$	+		$^{\mathrm{Nb}_{2}\mathrm{O}_{4}}$	+		Cr <sub>2</sub> O <sub>3</sub>	-2197
8	V	+	€	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	v <sub>2</sub> 0 <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	-2170
2	Er	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+		Er <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-2113
3	Ca	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+	3	CaO	+		Cr <sub>2</sub> O <sub>3</sub>	-2044
3	Th	+	4	Ba(CrO <sub>4</sub> )	=	4	BaO	+	3	ThO 2	+	2	Cr <sub>2</sub> 0 <sub>3</sub>	-2030
3	Ве	+	2	Na <sub>2</sub> (CrO <sub>4</sub> )	***	2	$Na_2O$	+	3	BeO	+		Cr 203	-2022
8	Cr	+	б	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Cr <sub>2</sub> O <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	-2011
2	La	+	2	$Ba(CrO_4)$	=	2	BaO	+		La <sub>2</sub> 03	+		Cr <sub>2</sub> O <sub>3</sub>	-1976
3	Hf	+		Ba(CrO <sub>4</sub> )	<b>33</b>	4	BaO	+	3	Hf0 <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-1966
2	Tb	+	2	$Ba(CrO_4)$	=	2	BaO	+		Tb2O3	+		Cr <sub>2</sub> O <sub>3</sub>	-1927
2	Nd	+	2	$Ba(CrO_4)$	=	2	BaO	+		$Nd_2O_3$	+		Cr <sub>2</sub> O <sub>3</sub>	-1915
2	D.L.	+		Ba(CrO <sub>4</sub> )	2	2	BaC	+		Pr <sub>2</sub> 0 <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-1912
4	Mn	۲	2	Pb(CrO4)	=		Pb <sub>2</sub> O	4.	4	MnO	+		Cr <sub>2</sub> O <sub>3</sub>	-1904
2	Sm	+	2	Ba(CrO <sub>4</sub> )	==	2	BaO	+		Sm <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-1897
6	Li	+	2	$Ag_2(CrO_4)$	<b>=</b>	2	Ag <sub>2</sub> O	+	3	L1 20	+		Cr <sub>2</sub> O <sub>3</sub>	-1894
4	Sr	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	4	SrO	+		Cr <sub>2</sub> O <sub>3</sub>	-1894
2	Gđ	+	2	Ba(CrO <sub>4</sub> )	=	2	BaO	+		Gd <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-1890
2	Ce	+	2	Ba(CrO <sub>4</sub> )	=	2	BaO	+		Ce <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-1870
6	Ta	+	10	$Ag_2(CrO_4)$	=	10	Ag <sub>2</sub> O	+	3	Ta 205	+	5	Cr <sub>2</sub> O <sub>3</sub>	-1861
3	Zr	+	4	$Ba(CrO_4)$	=	4	BaO	+	3	ZrO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-1799
2	Sc	+	2	Ba(CrO <sub>4</sub> )	=	2	BaO	+		Sc 203	+		Cr <sub>2</sub> O <sub>3</sub>	-1782

Table 33 (cont.)

Reaction	Enthalpy, cal/cc
1 2 2 2 4 7 2 Cr O	-1768
$2 \text{ La} + 2 \text{ Na}_{2}(\text{CrO}_{4}) = 2 \text{ Na}_{2}\text{O} + 2 \text{ La}_{2}\text{O}_{3} + 2 \text{ Cr}_{2}\text{O}_{3}$ $6 \text{ Nb} + 8 \text{ Ag}_{2}(\text{CrO}_{4}) = 8 \text{ Ag}_{2}\text{O} + 3 \text{ Nb}_{2}\text{O}_{4} + 4 \text{ Cr}_{2}\text{O}_{3}$	-1749
$2 \text{ V} + 2 \text{ Ag}_{2}(\text{CrO}_{4}) = 2 \text{ Ag}_{2}\text{O} + \text{V}_{2}\text{O}_{3} + \text{Cr}_{2}\text{O}_{3}$	-1732
$3 \text{ Hf} + 4 \text{ Na}_2(\text{CrO}_4) = 4 \text{ Na}_2\text{O} + 3 \text{ HfO}_2 + 2 \text{ Cr}_2\text{O}_3$	-1722
$8 Ga + 6 Pb(CrO_4) = 3 Pb_2O + 4 Ga_2O_3 + 3 Cr_2O_3$	-1711
$2 \text{ Nd} + 2 \text{ Na}_{2}(\text{CrO}_{4}) = 2 \text{ Na}_{2}\text{O} + \text{ Nd}_{2}\text{O}_{3} + \text{ Cr}_{2}\text{O}_{3}$	-1705
$2 \text{ Sm} + 2 \text{ Na}_{2}(\text{Cro}_{4}) = 2 \text{ Na}_{2}^{0} + 5 \text{m}_{2}^{0}_{3} + \text{Cr}_{2}^{0}_{3}$	-1684
$2 \text{ Gd} + 2 \text{ Na}_2(\text{Cro}_4) = 2 \text{ Na}_2\text{O} + \text{ Gd}_2\text{O}_3 + \text{ Cr}_2\text{O}_3$	-1679
2 4 2 Tr O	-1677
$3 \text{ Np} + 4 \text{ Ba}(\text{CrO}_4) = 4 \text{ BaO} + 3 \text{ NpO}_2 + 2 \text{ Cr}_2 \cdot 3$ $3 \text{ Sr} + 2 \text{ Ag}_2(\text{CrO}_4) = 2 \text{ Ag}_2 \cdot 0 + 3 \text{ SrO} + \text{ Cr}_2 \cdot 0_3$	-1676
$2 \text{ Al} + 2 \text{ Na}_{2}(\text{CrO}_{4}) = 2 \text{ Na}_{2}\text{O} + \text{Al}_{2}\text{O}_{3} + \text{Cr}_{2}\text{O}_{3}$	-1665
$8 p + 6 pb(cro_4) = 3 pb_2 + 4 p_2 + 3 cr_2 $	-1658
$2 \text{ Ti} + 2 \text{ Ba}(\text{CrO}_{4}) = 2 \text{ BaO} + \text{Ti}_{2}\text{O}_{3} + \text{Cr}_{2}\text{O}_{3}$	-1649
$4 \text{ Ba} + 2 \text{ Pb}(\text{CrO}_4) = \text{Pb}_2\text{O} + 4 \text{ BaO} + \text{Cr}_2\text{O}_3$	-1614
$2 \text{ Sc} + 2 \text{ Na}_2(\text{CrO}_4) = 2 \text{ Na}_2\text{O} + \text{ Sc}_2\text{O}_3 + \text{ Cr}_2\text{O}_3$	<b>-</b> 1370
$4 \text{ Zn} + 2 \text{ Pb}(\text{CrO}_4) = \text{Pb}_2\text{O} + 4 \text{ ZnO} + \text{Cr}_2\text{O}_3$	-1566
$3 \text{ Zr} + 4 \text{ Na}_2(\text{CrO}_4) = 4 \text{ Na}_2\text{O} + 3 \text{ ZrO}_2 + 2 \text{ Cr}_2\text{O}_3$	-1565
$3 \text{ Mn} + 2 \text{ Ag}_2(\text{CrO}_4) = 2 \text{ Ag}_2\text{O} + 3 \text{ MnO} + \text{Cr}_2\text{O}_3$	-1561
$3 \text{ Ba} + 2 \text{ Ag}_2(\text{CrO}_4) = 2 \text{ Ag}_2\text{O} + 3 \text{ BaO} + \text{Cr}_2\text{O}_3$	-1460
$2 \text{ Ga} + 2 \text{ Ag}_2(\text{CrO}_4) = 2 \text{ Ag}_2\text{O} + \text{ Ga}_2\text{O}_3 + \text{ Cr}_2\text{O}_3$	-1426
$2P + 2Ag_2(CrO_4) = 2Ag_2O + P_2O_3 + Cr_2O_3$	-1407
$3 \text{ Zn} + 2 \text{ Ag}_2(\text{CrO}_4) = 2 \text{ Ag}_2\text{O} + 3 \text{ ZnO} + \text{Cr}_2\text{O}_3$	-1330
$4 \text{ W} + 6 \text{ Pb}(\text{CrO}_4) = 3 \text{ Pb}_2\text{O} + 4 \text{ WO}_3 + 3 \text{ Cr}_2\text{O}_3$	-1329
$3 \text{ sr} + 2 \text{ Ba}(\text{CrO}_4) = 2 \text{ BaO} + 3 \text{ srO} + \text{ Cr}_2\text{O}_3$	-1 296
$3 \text{ Fe} + 2 \text{ Pb}(\text{CrO}_4) = \text{Pb}_2\text{O} + \text{Fe}_3\text{O}_4 + \text{Cr}_2\text{O}_3$	-1 230
$2 \text{ Sn} + 2 \text{ Pb}(\text{CrO}_4) = \text{Pb}_2\text{O} + 2 \text{ SnO}_2 + \text{Cr}_2\text{O}_3$	-1 206
$2 \text{ MO} + 2 \text{ Pb}(\text{CrO}_4) = \text{Pb}_2\text{O} + 2 \text{ MOO}_2 + \text{Cr}_2\text{O}_3$	-1198
$3 \text{ sr} + 2 \text{ Na}_2(\text{Cro}_4) = 2 \text{ Na}_2\text{O} + 3 \text{ srO}^2 + \text{Cr}_2\text{O}_3$	-1162
$W + 2 Ag_2(CrO_4) = 2 Ag_2O + WO_3 + Cr_2O_3$	-1136
$2 \text{ Al} + 2 \text{ K}_2(\text{CrO}_4) = 2 \text{ K}_2\text{O} + \text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$	-1113

Table 33 (cont.)

							React	ic	on					Enthalpy, cal/cc
2	Ge	+	2	Pb(CrO <sub>4</sub> )	<b>32</b>		Pb,0	+	2	GeO <sub>2</sub>	+		Cr <sub>2</sub> 03	-1095
9	Fе	+	8	Ag 2(CrO4)	=	8				Fe <sub>3</sub> O <sub>4</sub>	+	4	Cr <sub>2</sub> O <sub>3</sub>	-1076
3	Sn	+	4	Ag 2 (CrO4)	=	4	Ag <sub>2</sub> O	+	3	SnO <sub>2</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-1068
3	Ge	+	4	$Ag_2(CrO_4)$	=	4	Ag <sub>2</sub> O	+	3	GeO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	<del>-</del> 986
3	Ni	+	2	Pb(CrO <sub>4</sub> )	=	2	PbO	+	3	NiO_	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 933
3	Co	÷	2	Pb(CrO <sub>4</sub> )	=	2	PbO	+	3	CoO	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 903
3	Ni	+	2	Ag <sub>2</sub> (CrO <sub>4</sub> )	=	2	Ag <sub>2</sub> O	+	3	NiO	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 865
3	Cđ	+	2	Pb(CrO <sub>4</sub> )	=	2	PbO	+	3	CdO	+		Cr <sub>2</sub> O <sub>3</sub>	-859
3	Çđ	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+	3	CdO	+		Cr <sub>2</sub> O <sub>3</sub>	-806
4	Sb	+	4	Pb(CrO <sub>4</sub> )	=	4	PbO	+		Sb <sub>4</sub> 0 <sub>6</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	<b>-7</b> 73
2	As	+	2	Pb(CrO <sub>4</sub> )	=	2.	РЮ	+		As 203	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 739
3	Pb	+	2	Pb(CrO <sub>4</sub> )	=	2	P <sub>p</sub> O	+	3	PbO	+		Cr <sub>2</sub> O <sub>3</sub>	-611
3	Bi	+	2	Pb(CrO <sub>4</sub> )	==	2	РЮ	+	3	BiO	+		Cr <sub>2</sub> O <sub>3</sub>	-533
3	Te	+	4	Pb(CrO <sub>4</sub> )	=	4	рю	+	3	TeO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-417
3	Te	+	4	$Ag_2(CrO_4)$	=	4	Ag <sub>2</sub> O	+	3	TeO 2	+	2	Cr <sub>2</sub> O <sub>3</sub>	-407
3	Cu	+	2	Pb(CrO <sub>4</sub> )	=	2	PbO	+	3	CuO	+		Cr <sub>2</sub> O <sub>3</sub>	-406
6	Rb	+	2	Pb(CrO <sub>4</sub> )	22	2	РЮ	+	3	Rb <sub>2</sub> O	+		Cr <sub>2</sub> O <sub>3</sub>	-401
6	Rb	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+	3	Rb <sub>2</sub> O	+		Cr <sub>2</sub> O <sub>3</sub>	-399
	S	+	2	Pb(CrO <sub>4</sub> )	=	2	PbO	+		so <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-370
6	Cs	+	2	Pb(CrO <sub>4</sub> )	=	2	PbO	+	3	Cs <sub>2</sub> O	+		Cr <sub>2</sub> O <sub>3</sub>	-315
6	Tl	+	2	Pb(CrO <sub>4</sub> )	<b>23</b>	2	PbO	+	3	T1 20	+		Cr <sub>2</sub> O <sub>3</sub>	-314
6	Rb	+	2	Ba(CrO <sub>4</sub> )	=	2	BaO			Rb 20	+		Cr <sub>2</sub> Q <sub>3</sub>	- 20 2
6	Rb	+	2	Na <sub>2</sub> (CrO <sub>4</sub> )	=	2	Na <sub>2</sub> O	+	3	Rb <sub>2</sub> O	+		Cr <sub>2</sub> O <sub>3</sub>	-154
6	Rb	+		K <sub>2</sub> (CrO <sub>4</sub> )	=	2	к <sub>2</sub> о	+	3	Rb <sub>2</sub> O	+		$\operatorname{Cr}_{2}^{\circ}O_{3}$	-38

MOST ENERGETIC CHROMATE AND DICHROMATE REACTIONS WITH METALS, IN TERMS OF GRAVIMETRIC ENTHALPY

					Rea	act	ion							Enthalpy, cal/g
3	Ве	+	2	Na <sub>2</sub> (CrO <sub>4</sub> )	=	2	Na <sub>2</sub> O	+	3	Вео	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-77</b> 2
4	Ве	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	4	BeO	+		Cr <sub>2</sub> O <sub>3</sub>	
8	Li	+	2	Pb(CrO <sub>4</sub> )	=		Pb20	+	4	Li <sub>2</sub> 0	+		Cr <sub>2</sub> O <sub>3</sub>	-648
4	Mg	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	4	MgO	+		Cr <sub>2</sub> 0 <sub>3</sub>	-619
2	Al	+	2	$Na_2(CrO_4)$	=	2	Na <sub>2</sub> O	+		Al 203	+		Cr <sub>2</sub> O <sub>3</sub>	-614
4	Ca	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	4	CaO	+		Cr <sub>2</sub> O <sub>3</sub>	-611
2	Sc	+	2	$Na_2(CrO_4)$	=	2	$Na_2O$	+		Sc 203	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 590
8	Sc	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Sc 203	+	3	Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 565
3	Ве	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+	3	BeO	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 553
3	Ве	+	2	$Ba(CrO_4)$	==	2	BaO	+	3	BeO	+		Cr <sub>2</sub> O <sub>3</sub>	-546
б	Li	1	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+	3	Li <sub>2</sub> 0	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 5 26
3	Ca	+	2	Ag <sub>2</sub> (CrO <sub>4</sub> )	=	2	Ag <sub>2</sub> O	+	3	CaO	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 509
3	Mg	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+	3	MgO	+		Cr <sub>2</sub> O <sub>3</sub>	-509
8	La	+		Pb(CrO <sub>4</sub> )	==	3	Pb <sub>2</sub> O	+	4	La203	+	3	Cr <sub>2</sub> O <sub>3</sub>	-487
2	Zr	+	2	Pb(CrO <sub>4</sub> )	==		Pb <sub>2</sub> O	+	2	ZrO2	+		Cr <sub>2</sub> O <sub>3</sub>	-484
8	Ti	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Ti <sub>2</sub> O <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	-484
2	La	+	2	$Na_2(CrO_4)$	=	2	Na <sub>2</sub> O	+		La203	+		Cr <sub>2</sub> O <sub>3</sub>	-484
3	Zr	+	4	$Na_2(CrO_4)$	33	4	Na <sub>2</sub> O	+	3	ZrO2	+	2	Cr <sub>2</sub> O <sub>3</sub>	-478
2	Sc	+		$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+		Sc <sub>2</sub> 0 <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-471
8	Pr	+		Pb(CrO <sub>4</sub> )	<b>E</b>	3	Pb <sub>2</sub> O	+	4	Pr <sub>2</sub> O <sub>3</sub>	÷	3	Cr <sub>2</sub> O <sub>3</sub>	-467
8	Nd	+		Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Nd 203	+	3	Cr <sub>2</sub> O <sub>3</sub>	-460
8	Ce	+		Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Ce <sub>2</sub> O <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	<b>-4</b> 56
4	Sr	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	4	SrO	+		Cr <sub>2</sub> O <sub>3</sub>	-451
				$Na_2(CrO_4)$			-							
8	Er	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Er <sub>2</sub> O <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	-448
8	Но	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Ho 203	+	3	Cr <sub>2</sub> O <sub>3</sub>	-446
				$Ba(CrO_4)$										
8	Sm	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Sm 2 <sup>O</sup> 3	+	3	$Cr_2O_3$	-443
3	Sr	+	2	$Na_2(CrO_4)$	=	2	$Na_2O$	+	3	SrO	+		cr <sub>2</sub> o <sub>3</sub>	-437

Table 34 (cont.)

				Re	eac	tic	on							Enthalpy, cal/g
8	Tb	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Tb <sub>2</sub> O <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	-437
8	Gđ	+	6	Pb(Cr04)	=		_			$Gd_2O_3$				-435
2	Sm	+	2	$Na_2(CrO_4)$	=	2	Na <sub>2</sub> O	+		$sm_2O_3$	+		Cr <sub>2</sub> 0 <sub>3</sub>	-4 27
2	La	+	2	Ag <sub>2</sub> (CrO <sub>4</sub> )	=	2	Ag <sub>2</sub> 0	+		La <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-427
2	Нf	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	2	HfO <sub>2</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-4 27
2	Th	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	2	ThO <sub>2</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-422
2	Gđ	+	2	$Na_2(CrO_4)$	=	2	Na <sub>2</sub> O	+		$Gd_2O_3$	+		Cr <sub>2</sub> O <sub>3</sub>	-418
3	Zr	+	4	$Ag_2(CrO_4)$	=	4	Ag <sub>2</sub> O	+	3	ZrO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-413
2	Pr	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+		Pr <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-410
2	Ti	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+		Ti <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-409
2	Al	+	2	$K_2(CrO_4)$	=	2	к <sub>2</sub> 0	+		Al 203	+		Cr <sub>2</sub> O <sub>3</sub>	-408
3	Hf	+	4	$Na_2(CrO_4)$	=	4	Na <sub>2</sub> O	+	3	HfO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-406
2	Иd	+	2	Ag <sub>2</sub> (CrO <sub>4</sub> )	=	2	Ag <sub>2</sub> O	+		Nd <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-405
2	Се	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+		Ce 203	+		Cr <sub>2</sub> O <sub>3</sub>	-401
2	Er	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+		Er <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-398
2	La	+	2	$Ba(CrO_4)$	=	2	BaO	+		La <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-397
3	Sr	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+	3	SrO	+		Cr203	<b>-396</b>
2	Но	+	2	Ag <sub>2</sub> (CrO <sub>4</sub> )	=	2	Ag <sub>2</sub> O	+		HO203	+		Cr <sub>2</sub> O <sub>3</sub>	-396
2	Sm	+	2	$Ag_2(CrO_4)$	<del>=</del>	2	Ag <sub>2</sub> 0	+		Sm 203	+		Cr <sub>2</sub> O <sub>3</sub>	-391
2	Tb	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+		Tb2O3	+		$\operatorname{cr}_2 \circ_3$	-388
2	Gd	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> O	+		Gd 203	+		Cr <sub>2</sub> O <sub>3</sub>	-386
2	U	+		Ph(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	2	υ0 <sub>2</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-379
2	Pr	+	2	Ba(CrO <sub>4</sub> )	=	2	BaO	+		Pr <sub>2</sub> 0 <sub>3</sub>	+		$\operatorname{Cr}_2 \operatorname{O}_3$	-378
3	Th	+		$Ag_2(CrO_4)$	=	4	Ag <sub>2</sub> 0	+	3			2		-377
3	Hf	+	4	Ag <sub>2</sub> (CrO <sub>4</sub> )	=	4	Ag <sub>2</sub> O	+	3	HfO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-377
3	Zr	+	4	Ba(CrO <sub>4</sub> )	=	4	BaO	*	3	ZrO2	+	2	Cr <sub>2</sub> O <sub>3</sub>	~374
2	Nd	+	2	$Ba(CrO_4)$	=	2	BaO	+		Nd 203	+		Cr <sub>2</sub> O <sub>3</sub>	-372
				Ba(CrO <sub>4</sub> )									$\operatorname{Cr}_{2}^{\circ}O_{3}^{\circ}$	
2	Ti	+	2	Ba(CrO <sub>4</sub> )	=									
				Ba(CrO <sub>4</sub> )									Cr <sub>2</sub> O <sub>3</sub>	
	Sm			Ba(CrC <sub>4</sub> )										

Table 34 (cont.)

_			-		Rea	ict1	on							Enthalpy cal/q
2	Tb	+	2	Ba(CrO <sub>4</sub> )	=	2	BaO	+		Tb <sub>2</sub> O <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-352
2	Gđ	+	2	Ba(CrO <sub>4</sub> )	=	2	BaO	+		Gd <sub>2</sub> C <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-350
4	Ba	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	4	BaO	+		Cr <sub>2</sub> O <sub>3</sub>	-350
8	V	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> 0	+	4	$v_{2}^{0}_{3}$	+	3	Cr <sub>2</sub> 0 <sub>3</sub>	-347
3	U	+	4	$Ag_2(CrO_4)$	=	4	Ag <sub>2</sub> 0	+	3	υ0 <sub>2</sub>	<i>÷</i>	2	Cr <sub>2</sub> O <sub>3</sub>	-341
3	Th	+	4	Ba(CrO <sub>4</sub> )	=	4	BaO	+	3	ThO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-341
3	Hf	+	4	Ba(CrO <sub>4</sub> )	=	4	BaO	+	3	HfO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-337
2	qN	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> U	+	2	NpO <sub>2</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-336
8	P	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	P203	+	3	Cr <sub>2</sub> O <sub>3</sub>	-336
2	Ир	÷	2	Pb(CTO <sub>4</sub> )	=		Pb <sub>2</sub> O	+		Nb204	+		Cr <sub>2</sub> O <sub>3</sub>	-3 28
3	Ba	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	+	3	BaO	+		Cr <sub>2</sub> O <sub>3</sub>	-320
8	Cr	+	6	Pb(CrO <sub>4</sub> )	=	3	Pb <sub>2</sub> O	+	4	Cr <sub>2</sub> O <sub>3</sub>	+	3	Cr <sub>2</sub> 7 <sub>3</sub>	-312
3	Ŋр	+	4	$Ag_2(CrO_4)$	22	4	Ag <sub>2</sub> 0	+	3	NpO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-307
2	V	+	2	Ag (0:04)	=	2	Ag <sub>2</sub> O	+		$v_{2}^{0}_{3}$	+		Cr <sub>2</sub> O <sub>3</sub>	-305
8	Ta	+	10	Pb(CrO <sub>4</sub> )	=	5	$Pb_2O$	+	4	$Ta_2O_5$	+	5	Cr <sub>2</sub> O <sub>3</sub>	-304
2	P	+	2	Ag2(CrO4)	3	2	Ag <sub>2</sub> 0	+		P 203	+		Cr <sub>2</sub> O <sub>3</sub>	- 294
4	Mn	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> O	+	4	MnO	+		Cr <sub>2</sub> O <sub>3</sub>	- 29 2
6	Иb	٠	8	$Ag_2(CrO_4)$	=	8	Ag <sub>2</sub> O	+	3	$^{\mathrm{Nb}_2\mathrm{O}_4}$	+	4	Cr <sub>2</sub> O <sub>3</sub>	- 29 2
6	Ta	+	10	Ag (CrO4)	=	10	A920	4*	3	Ta 205	+	5	Cr <sub>2</sub> O <sub>3</sub>	- 277
8	GT	+	6	Pb(CrO <sub>4</sub> )	æ	3	Pb <sub>2</sub> O	+	4	Ga <sub>2</sub> O <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	-275
3	Mn	+	2	$Ag_2(CrO_4)$	23	2	Ag <sub>2</sub> O	÷	3	MnO	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-</b> 265
3	Np	+		$Ba(CrO_4)$		4	BaO	*	3	NpO <sub>2</sub>	<b>*</b>	2	$\operatorname{Cr}_2 \operatorname{O}_3$	- 258
2	Ga	+	2	$Ag_2(CrO_4)$	=	2	Ag <sub>2</sub> 0	÷		$Ga_2O_3$	+		Cr2O3	- 251
4	Zn	+		Pb(CrO <sub>4</sub> )									Cr <sub>2</sub> O <sub>3</sub>	- 240
3	Zn	+	2	Ay2(CrO4)	=	2	Ag <sub>2</sub> 0	÷	3	ZnO	+		Cr <sub>2</sub> O <sub>3</sub>	- 225
3	Fe	+	2	Pb(CrO <sub>4</sub> )	<b>=</b>		Pb <sub>2</sub> O	+		Fe3O4	+		$\operatorname{Cr}_2 \circ_3$	-187
2	Sn	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> 0	+	2	SnO <sub>2</sub>	+		$\operatorname{Cr}_2\operatorname{O}_3$	-184
9	Fe	+	8	Ag <sub>2</sub> (CrC <sub>4</sub> )	æ	8	Ag 20	+	3	Fe <sub>3</sub> O <sub>4</sub>	+	4	Cr <sub>2</sub> O <sub>3</sub>	-162
ţ:}	Зn	٠.	4	Ag <sub>2</sub> (CrO <sub>4</sub> )	9	4	Ag <sub>2</sub> 0	+	3	SnO <sub>2</sub>	+	2	Cr <sub>2</sub> 0 <sub>3</sub>	-180
2	Ge	+	2	Pb(CrO <sub>4</sub> )	=		Pb <sub>2</sub> 0	+	2	GeO $_2$	+		Cr <sub>2</sub> O <sub>3</sub>	-179
3	Se	+	4	Ag 2 (CrO4)	=	4	Ag <sub>2</sub> O	+	3	GeO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-176
2	Mo	+	2	Pb(Cro <sub>4</sub> )	=		Pb <sub>2</sub> O	+	2	MoO <sub>2</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-173

Table 34 (cont.)

_			****	Read	:t:	ion			·····				Enthalpy, cal/g
4	W	+	6 Pb(CrO <sub>4</sub> )	= (	3 1	Pb <sub>2</sub> 0	+	4	wo <sub>3</sub>	+	3	Cr <sub>2</sub> O <sub>3</sub>	-171
1	W	+	2 Ag <sub>2</sub> (CrC <sub>4</sub> )	= ;	2 2	Ag <sub>2</sub> 0	+		wo3	+		Cr <sub>2</sub> 0 <sub>3</sub>	-170
6	Rb	+	2 Ag <sub>2</sub> (CrO <sub>4</sub> )	=	2 2	Ag <sub>2</sub> 0	+	3	Rb <sub>2</sub> O	+		Cr <sub>2</sub> 0 <sub>3</sub>	-153
6	Rb	+	2 Pb(CrO <sub>4</sub> )	=	2 1	PbO	+	3	Rb <sub>2</sub> O	+		Cr <sub>2</sub> O <sub>3</sub>	-151
3	Ni	+	2 Ag <sub>2</sub> (CrO <sub>4</sub> )	= ,	2 2	Ag <sub>2</sub> 0	+	3	NiO	+		Cr <sub>2</sub> O <sub>3</sub>	-141
3	Ni	+	2 Pb(CrO <sub>4</sub> )	=	2 1	Pb0	+	3	NiO	+		Cr <sub>2</sub> 0 <sub>3</sub>	-138
3	Co	+	2 Pb(CrO <sub>4</sub> )	25	2 1	PbO	+	3	CoO	+		Cr <sub>2</sub> 0 <sub>3</sub>	-134
3	Cd	+	2 Ag <sub>2</sub> (CrO <sub>4</sub> )	=	2 2	Ag <sub>2</sub> 0	+	3	CGO	+		Cr <sub>2</sub> 0 <sub>3</sub>	-1 26
3	Cđ	+	2 Pb(CrO <sub>4</sub> )	=	2 1	PbO	+	3	CdO	+		Cr <sub>2</sub> 0 <sub>3</sub>	-1 23
4	Sb	+	4 Pb(CrO <sub>4</sub> )	= 4	1	PbO	+		Sb <sub>4</sub> 0 <sub>6</sub>	+	2	Cr <sub>2</sub> 0 <sub>3</sub>	-120
2	As	+	2 Pb(CrO <sub>4</sub> )	22	2 1	РЬО	+		As 203	+		Cr <sub>2</sub> 0 <sub>3</sub>	-119
6	Cs	+	2 Pb(CrO <sub>4</sub> )	=	2 1	Pb0	+	3	Cs <sub>2</sub> O	+		Cr <sub>2</sub> 0 <sub>3</sub>	-115
6	Rb	+	2 Ba(CrO <sub>4</sub> )	=	2	BaO	+	3	Rb <sub>2</sub> O	+		Cr <sub>2</sub> O <sub>3</sub>	-88
6	Rb	+	2 Na <sub>2</sub> (CrO <sub>4</sub> )	=	2 1	Na 20	+	3	Rb <sub>2</sub> O	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-8</b> 3
3	Pb	+	2 Pb(CrO <sub>4</sub> )	=	2 1	Pb0	+	3	₽50	+		Cr <sub>2</sub> O <sub>3</sub>	<b>-7</b> 5
3	Te	+	4 Ag <sub>2</sub> (CrO <sub>4</sub> )	= (	1 3	Ag <sub>2</sub> 0	+	3	TeO <sub>2</sub>	+	2	Cr <sub>2</sub> O <sub>3</sub>	-70
3	Bi	+	2 Pb(CrO <sub>4</sub> )	3	2 1	Pb0	+	3	BiO	+		Cr <sub>2</sub> O <sub>3</sub>	-69
3	Te	+	4 Pb(CrO <sub>4</sub> )	<b>=</b>	1 1	Pb0	+	3	TeO 2	+	2	Cr <sub>2</sub> O <sub>3</sub>	-66
	S	+	2 Pb(CrO <sub>4</sub> )	<b>2</b>	2	PbO	+		so <sub>3</sub>	+		Cr <sub>2</sub> O <sub>3</sub>	-64
3	Cu	+	2 Pb(CrO <sub>4</sub> )	=	2	PLO	+	3	CuO	÷		Cr <sub>2</sub> 0 <sub>3</sub>	-60
6	Tl	+	2 Pb(CrO <sub>4</sub> )	<b>=</b>	2 1	P <sub>b</sub> O	+	3	T1 20	+		Cr <sub>2</sub> O <sub>3</sub>	-34
6	Rb	+	2 K <sub>2</sub> (CrO <sub>4</sub> )	=	2 1	к <sub>2</sub> 0	+	3	Rb <sub>2</sub> O	+		Cr <sub>2</sub> O <sub>3</sub> ,	- 20

Table 35

VOLUMETRIC ENTHALPIES (cal/cc) OF REACTIONS OF METALS

WITH CHROMATES AND DICHROMATES

(In descending order from top to bottom and left to right)

<del></del>	<del></del>				·
Metal	PbCr0 <sub>4</sub>	Ag2CrO4	BaCrO <sub>4</sub>	Na <sub>2</sub> CrO <sub>4</sub>	K2CrO4
Вe	-3845	-2881	-2293	-2022	
U	-3322	-2546			
H£	-3310	-2543	-1966	-1722	
$\mathtt{Th}$	-3 259	-2563	-2030		
Но	_3173	-25 29			
Zr	-3065	_2377	_1799	-1565	
Tb	-3048	-2439	_1927	1000	
La	-3046	-2464	-1976	-1768	
en En	-2999 3008	-2406	-1897	-1684	
nd Gd	-2998 2086	-2415 -2398	-1915	-1705	
Fr	-2986 -2980	-2398 -2408	-1890 -1912	-1679	
Ce	-2939	-2371	-1870		
95 q%	-2914	-2265	-1677		
Mg	-2907	-2348	-1011		
Sc	-2879	-2303	-1782	-1570	
Ti	-2861	-2233	-1649	2070	
Er	-2499	-2113			
Ca	-2393	-2044			
Ta	-2377	-1861			
Li	<b>-2</b> 203	-1894			
Nb	-2197	-1749			
V	-2170	-1732			
Cr	-2011				
Mn	-1904	-1551			
Sr	1894	-1676	-1 296	-116?	
Al				-1665	-1113
ā	-1.658	-1407			
Ba	-1614	-1460			
Zn	-1566	-1330			
Ga	1711	-1426			
W Fe	1329	-1136			
Sn	-1 230 -1 206	-1076 -1068			
No	1198	-1000		•	
Ge	1095	-986			
Ni	<u>-933</u>	_865			
Co	<u> -903</u>	-045			
Cd	-859	-806			
Sb	-773				
λs	<del>-</del> 739				
Pb	-611				
Bi	-533				
Тe	-417	-407			
Ĉu	-406	- 401			
Rb	-401	-399	- 202	-154	-38
5	-370	- • •	- <b></b>	_ · ·	
Ċs	-315				
Tl	-314				

Table 36

GRAVIMETRIC ENTHALPIES (cal/g) OF REACTIONS OF METALS
WITH CHROMATES AND DICHROMATES
(In descending order from top to bottom and left to right)

Metal	Na <sub>2</sub> CrO <sub>4</sub>	PbCrO4	Ag <sub>2</sub> Cr0 <sub>4</sub>	BaCrO <sub>4</sub>	K2CrO4
Be	-772	-687	-553	-546	
Li		-648	-526	3.0	
Mg		-619	-509		
Al	-614				-408
Ca		-611	-509		100
Sc	-590	-565	-471	-443	
La	-484	-487	-427	-397	
Zr	-478	-484	-413	-374	
Ti	- 1,75	-484	-409	-366	
Pr		-467	-410	-378	
Nd	-449	-460	-405	-372	
Ce		-456	~401	- 367	
Sr	-437	-451	-396	-360	
Er		-448	-398	-300	
Ho		-446	-396		
2m	-427	-443	-391	<b>∽</b> 356	
Tb		-437	-388	~352	
ĞĞ	-418	-435	-386	-350	
H£	-406	-427	-377	-337	
Th	-400	-422	-377	-341	
Ü		-379	-341	3 4 2	
Ba		-350	-320		
Λ		-347	-305		
qИ		-336	-307	- 258	
p		-336	- 294	- 250	
йb		-328	- 29 2		
Cr		-312	-234		
Ta		-304	- 277		
NO.		-292	- 265		
Ga		-275	- 25 l		
Zn		-240	- 23X - 225		
24		-187	-182		
Sn .		-184	-180		
Ge		-179	-176		
Mo		-173	~710		
W W		-171	-170		
Яb	-83	-151	-153	-88	- 20
NI IN	-04	-138	-133 -141	-00	- 40
Co		-134	~747		
ca			-126		•
		-123	-7.50		
Sb		-1 20			
As		-119			
Cs		-115			
5р		_75			
Te		-66	-70		
Bi		-69			
S		_64			
Cu		-60			
Tl		_34			
_					

## K. Boride Reactions

The reactions of 3 metals with 8 borides resulted in 14 reactions. Although the properties for only a few reactions were calculated, they are of interest because of the refractory nature of the products and reactants. Some representative reactions are shown in Table 37, and the volumetric and gravimetric enthalpies of all the boride reactions are listed in Tables 38 and 39. Except for boron carbide, the enthalpies are low. However, the reactions of titanium and zirconium with boron carbide are energetic. It would be interesting to examine these reactions experimentally to determine the effect of the refractoriness of the reactants and products on the behavior of the reactions.

Table 37

DATA ON REACTIONS OF VARIOUS METALS WITH BORIDES

	4 N +	CB <sub>4</sub> =	+ 0	4 NB
Heat of formation Molecular Weight	14.01	12.20 55.29 2.50	12.01 2.25	60.30 24.83 2.20 3000.00
Melting point, °C Boiling point, °C Heat of reaction, kcal	-229.00 1.22	2450.00 3500.00	4347.00	
Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc	-2057.10 -2503.76			
	2 Ti +	CB₄ =	+ v	2 TiB2
Heat of formation	47.90	12.20	12.01	70.00 69.54
ar weign	4.50	2.50 2450.00	2.25	4. C • 4.
Melting point, oc Boiling point, oc	3000.00	3500.00	4347.00	
700.000	3.48 -845.85 -2944.37			
			+	0 2rB
	2 Zr +	CB₄ =	+ ا	2 41 B 2
Heat of formation Molecular Weight	91.22	12.20	12.01	76.40 112.86 6.08
point,	1852.00	2450.00 3500.00	4347.00	
Boiling point, °C Heat of reaction, kcal	_140.60 _4.70			
Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc	_591.43 _2777.43			

Table 37 (cont.)

	2 N +	TiB <sub>2</sub> =	Ti +	2 NB
Heat of formation Molecular weight Density	14.01	70.00 69.54 4.5	47,90 4,50 1812.00	-60,30 24.83 2.20 3000,00
אונונ	-50.60 1.95 -518.68			
	5 N +	Ti <sub>2</sub> B <sub>5</sub> =	2 Ti +	5 NB
formati ar weigh	14.01	10500 149.90 4.63	47,90 4,50 1812,00	-60,30 24.83 2.20 3000.00
Melting point, "C Boiling point, "C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/cc	-196.50 1.85 -893.43 -1650.44		3000.00	
	5 Zr +	2 Ti2B5 =	4 Ti +	5 ZrB <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	91.22 6.40 1852.00 2900.00 -172.00 5.56 -227.54	-105.00 149.90 4.63	47.90 4.50 1812.00 3000.00	-76.40 112.86 6.08

Table 38

VOLUMETRIC ENTHALPIES (cal/cc) OF REACTIONS OF METALS WITH BORIDES (In descending order from top to bottom and left to right)

Metal	CB <sub>4</sub>	Ti <sub>2</sub> B <sub>5</sub>	TiB <sub>2</sub>	ZrB <sub>2</sub>	TiB	~ · · · · · · · · · · · · · · · · · · ·
Ti	-2944					
N	-2503	-1650	-1037	- 830	- 804	
Zr	-2777	-1264	- 221		- 110	

Table 39

GRAVIMETRIC ENTHALPIES (cal/g) OF REACTIONS OF METALS WITH BORIDES (In descending order from top to bottom and left to right)

								• • • • • • • • • • • • • • • • • • • •
Metal	CB <sub>4</sub>	ZrBi2	Ti <sub>2</sub> B <sub>5</sub>	TiB <sub>2</sub>	TiB	ZrB <sub>2</sub>	Ti <sub>2</sub> B	ZrB
N	-2057	-1551	- 893	- 518	- 334	- 313	- 201	- 183
Ti	- 845	- 277			- 20		•	
Zr	- 591		- 227	- 39				

# L. Phosphide Reactions

A total of 25 phosphides and 500 reactions was surveyed. The phosphides do not form an energetic class of reactions. The most energetic revealed in these studies,

$$15 \text{ Mg} + 2 \text{ N}_3 \text{P}_5 = 6 \text{ N} + 5 \text{ Mg}_3 \text{P}_2,$$

yields only -1439 cal/cc. A few representative reactions are shown in Table 40.

Table 40

DATA ON REACTIONS OF VARIOUS METALS WITH PHOSPHIDES

	9 Mg	+	2 Au <sub>2</sub> P <sub>3</sub>	н	4 Au	+	3 Mg <sub>3</sub> P <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	24.32 1.74 650.00 11.20.00 -3.35.00 4.39 -281.34		-24.10 487.34 6.67		197,00 19.30 1063.00 2660.00		134.91
	3 Mg	+	Ba <sub>3</sub> P <sub>2</sub>	ıı	3 Ba	+	Mg <sub>3</sub> P <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	24.32 1.74 650.00 1120.00 -10.00		474.03		137.36 3.50 704.00 1638.00		134.91
	3 Mg	+	Ca <sub>3</sub> P <sub>2</sub>	u	3 Ca	+	Mg <sub>3</sub> P <sub>2</sub>
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	24.32 3.74 650.00 1120.00 -7.50 2.07 -29.39		-120.50 182.20 2.24 1600.00		40.08 1.55 850.00 1240.00		-128 00 134.91

Table 40 (cont.)

	3 Mg	+	2 Cu <sub>3</sub> P	ıţ	6 Cu	+	$Mg_3P_2$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	24.32 1.74 650.00 1120.00 -55.20 4.64 -106.94		-36.40 221.60 6.40		63.54 8.92 1083.00 2582.00		134.91
	3 Mg	+	CuP <sub>2</sub>	Į.	Cu	+	$Mg_3P_2$
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g	24.32 1.74 650.00 1120.00 -99.10		125.49		63.54 8.92 1083.00 2582.00		134.91
	3 Mg	+	2 FeP	11	2 Fe	+	Mg 3 P 2
Heat of formation Molecular weight Density Melting point, °C Boiling point, °C Heat of reaction, kcal Reactants' density Gravimetric enthalpy, cal/g Volumetric enthalpy, cal/c	24,32 1,74 650.00 1120.00 -72.00 3,27 -291,95		-28.00 86.83 5.20		55,85 7,86 1535,00 2800,00		-128.00 134.91

### M. Organic Fluoride Reactions

A limited survey was made of the reactions of organic fluorides with metals. The properties were tabulated for 76 organic fluorides for which data on heat of formation were available. These included perfluorinated compounds, partially fluorinated hydrocarbons, mixed halogenated organics, and organics containing various combinations of hydrogen, oxygen, nitrogen and fluorine. The enthalpies of reactions of 89 metals\* with carbon tetrafluoride and hexafluoroethane were calculated. Both of these compounds are effective oxidizers.

The volumetric enthalpies for the 30 most energetic reactions of each fluoride are listed in Tables 41 and 42. Each reaction is represented by the metal reactant and the product fluoride. The Group IIA metals (beryllium, magnesium, calcium, strontium, and barium), the Group IVB metals (titanium, zirconium, and hafnium), and the rare earth metals (yttrium, lanthanum, neodymium, praseodymium, uranium, and thorium) are very energetic with these fluorides.

In this instance each valence state of a metal is considered as a separate unit.

Table 41  $\begin{tabular}{ll} \begin{tabular}{ll} \begin{tabular$ 

Reaction	Product	Enthalpy cal/cc
Be	BeF <sub>2</sub>	-5.75
Y	YF <sub>3</sub>	-5.14
La	LaF3	-5.02
М	NdF3	-4.98
Pr	PrF3	-4.97
U	UF <sub>3</sub>	-4.74
Mg	MgF <sub>2</sub>	-4.73
H£	HfF3	-4.54
ט	UFA	-4.53
Th	ThF	-4.50
Sc	Scr	-4.47
2r	ZrF3	-4.46
2r	ZrFA	-4.45
H£	HEF	-4.36
Li	Lif	-4.18
Ca	CaF <sub>2</sub>	-4.14
Ti	Tif	-4.07
Th	ThF <sub>3</sub>	-4.05
Ce	CeF3	-4.05
Al	Alf	-4.04
H£	HEF <sub>2</sub>	-3.92
U	۷Fς	-3.85
Zr	ZrF <sub>2</sub>	-3.84
v	VF <sub>2</sub>	-3.59
Ti	TiF4	-3.48
В	BF <sub>3</sub>	-3.47

Table 41 (cont.)

Reaction	Product	Enthalpy, cal/cc
Si	SıF <sub>4</sub>	-3.42
Mn	MnF <sub>2</sub>	-3.36
Ti	TiF <sub>2</sub>	-3.32
Ce	CeF <sub>4</sub>	-3.30
v	VF <sub>3</sub>	-3.29
Cr	CrF <sub>3</sub>	-3.26
Ba	BaF <sub>2</sub>	-3.23
U	ur <sub>6</sub>	-3.16
Cr	CrF <sub>2</sub>	-3.15
Ta	TaF3	-2.90
v	VF <sub>4</sub>	-2.83
Zn	ZnF <sub>2</sub>	-2.82
Ta	TaF2	-2.80
Ga	Gar <sub>3</sub>	-2.75
Na	NaF	-2.67
Mn	MnF3	-2.63
Fe	FeF <sub>3</sub>	-2.59
Ni	NiF <sub>2</sub>	-2.53
Co	CoF <sub>2</sub>	-2.51
In	InF <sub>3</sub>	-2.45
Ge	GeF <sub>2</sub>	-2.34
Cd	CdF <sub>2</sub>	-2.25
Cr	CrF4	-2.22
Ta	TaF5	-2.19
Ga	GaF <sub>2</sub>	-2.18
Cr	CrF <sub>5</sub>	-2.16
	~	

Table 41 (cont.)

Reaction	Product	Enthalpy, cal/cc
W	wf <sub>6</sub>	-2.09
In	InF <sub>2</sub>	-1.97
Mo	MoF <sub>6</sub>	-1.96
Nb	NbF <sub>5</sub>	-1.94
V	VF <sub>5</sub>	-1.91
Ge	GeF₄	-1.91
Sn	SnF <sub>2</sub>	-1.89
Мо	MoF <sub>5</sub>	-1.89
Pb	PbF <sub>2</sub>	-1.83
Bi	B <sub>±</sub> F <sub>4</sub>	-1.76
Sb	SbF <sub>3</sub>	-1.75
N	NF <sub>3</sub>	-1.70
Bi	BiFa	-1.64
K	KF	-1.63
Мо	MoF <sub>4</sub>	-1.62
Co	.CoF3	-1.53
W	WF <sub>4</sub>	-1.52
Fe	FeF <sub>2</sub>	-1.50
Sn	SnF <sub>4</sub>	-1.50
Cu	CuF <sub>2</sub>	-1.47
Rb	RbF 2	-1.34
Sb	SbF <sub>5</sub>	-1.31
Bi	BiF <sub>2</sub>	-1.30
Mn	MnF	-1.22
W	WF <sub>5</sub>	-1.16
	•	

Table 42  $\begin{tabular}{ll} \begin{tabular}{ll} \begin{tabular$ 

Reaction	Product	Enthalpy, cal/cc
Ве	BeF <sub>2</sub>	-5.14
X,	YF <sub>3</sub>	-4.69
La	LaF <sub>3</sub>	-4.57
Nd	NdF <sub>3</sub>	-4.57
Pr	PrF <sub>3</sub>	-4,51
Μς <sub>j</sub>	MgF <sub>2</sub>	-4.24
${f v}$	UF <sub>3</sub>	-4.167
Th	ThF <sub>4</sub>	-3.94
Sc	ScF <sub>3</sub>	-3.93
ŭ	UF <sub>4</sub>	-3.90
Zr	ZrF <sub>4</sub>	-3.83
Li	Lif	-3.82
Ca	$\mathtt{CaF}_2$	-3.75
H£	HfF <sub>4</sub>	-3.72
Ce	CeF <sub>3</sub>	-3.64
Th	ThF3	-3.52
14	AlF <sub>3</sub>	-3.37
Sr	SrF <sub>2</sub>	-3.23
บ	UF <sub>5</sub>	-3.14
V	VF <sub>2</sub>	-2.93
Ba	BaF <sub>2</sub>	-2.88
Ce	CeF <sub>4</sub>	-2.76
Ti	TiF <sub>4</sub>	-2.73
Si	SiF <sub>4</sub>	-2.68
В	BF <sub>3</sub>	-2.66
Mn	MnF,	-2.65
V	VF <sub>3</sub>	-2.54

Table 42 (cont.)

Reaction	Product	Enthalpy, _cal/cc
Cr	CrF <sub>3</sub>	-2.48
Cr	CrF <sub>2</sub>	-2.42
ŭ	UF <sub>6</sub>	2.36
Na	NaF	-2.33
Ta	$\mathtt{TaF}_3$	-2.16
Ta	TaF <sub>2</sub>	-2.12
Zn	ZnF <sub>2</sub>	-2.12
Ga	$\operatorname{GaF}_3$	-2.00
V	VF <sub>4</sub>	-1.99
Mn	MnF <sub>3</sub>	-1.80
Fe	FeF3	-1.75
In	InF <sub>3</sub>	-1.75
Ni	NiF <sub>2</sub>	-1.73
Co	CoF <sub>2</sub>	-1.71
Au	Auf .	-1.71
Cd	CdF <sub>2</sub>	-1.58
Au	. AuF	-1.45
K	K£ 3	-1.41
Os	OsF <sub>8</sub>	-1.39
Os	Osf <sub>6</sub>	-1.35
In	InF <sub>2</sub>	-1.33
Cr	CrF <sub>4</sub>	-1.31
Ta	TaFs	-1.30
Sn	SnF <sub>2</sub>	-1.26
Pb	PbF <sub>2</sub>	-1.22
Cr	CrF <sub>5</sub>	-1.22
Ge	GeF <sub>4</sub>	-1.56
Rb	RbF	-1.14

<u>.</u>

Table 42 (cont.)

_		Enthalpy,	
Reaction	Product	_cal/cc_	
Nb	NbF <sub>5</sub>	-1.03	
Sb	SbF <sub>3</sub>	-1.03	
Мо	MoF <sub>6</sub>	-1.01	
Bi	BiF <sub>4</sub>	-1.01	
V	VF <sub>5</sub>	-1.01	
Bi	BiF <sub>3</sub>	95	
Mo	MoF <sub>5</sub>	<b></b> 95	
Cs	CsF	88	
Mo	MoF	69	
Sn	SnF	66	
Fe	FeF <sub>2</sub>	64	
Cu	CuF <sub>2</sub>	60	
W	Wf <sub>4</sub>	58	
Co	CoF <sub>3</sub>	58	
Σn	InF	57	
Sb	SbF <sub>5</sub>	43	
Tl	TIF	37	
Ou	CuF	30	
Ag	AqF	28	

### IV. ENTHALPY BEHAVIOR PATTERNS

The groups examined in the present study are compared in Table 43 according to the energy of their reactions. The most meaningful comparison would involve reactions between one metal and the compounds of another metal, e.g., the reactions of magnesium with the carbide, nitride, oxide, fluoride, silicide, phosphide, and sulfide of lithium. Because of the limited data available, however, the values in Table 43 apply to reactions of the metals with different compounds in each system. These compounds are listed at the top of each column.

Table 43

COMPARISON OF THE REACTION ENERGIES OF THE GROUPS STUDIED

		7	Volumetric	Enthalpy,	kcal/cc	-
Family	Group IV	Group V		Group VI		
2	Li <sub>2</sub> C <sub>2</sub>	Fe <sub>2</sub> N	Ba(N <sub>3</sub> ) <sub>2</sub>	LiNO3	CoF3	
Be Mg		-2.4 -1.3	-3.3 -1.3	-7.8 -5.0	-5.1 -4.1	
Al Ta	-0.1 -2.5	-1.9 -1.8	-2.5 -2.5	-6.4 -5.1	-3.0 -1.8	
Ba Th	-0.6	-0 -2.2	-2.6	-2,2 -5,9	-2.8 -3.8	
3	CoSi <sub>2</sub>	1	N <sub>3</sub> P <sub>5</sub>	FeS <sub>2</sub>	CoCl <sub>2</sub>	WCl <sub>4</sub>
Be Mg Al Ta Ba Th	-0.1 - -5.1		-1.4	-2.1 -2.4 -1.2 -1.4 -3.2	-1.2 -1.5 '-1.0 -1.7 -1.4	-2.2 -2.4 -1.8 -1.1 -2.3 -2.4

The oxide and fluoride reactions tend to be the most energetic. The nitrates and nitrites are included in the oxide system since the reaction products are invariably oxides. The nitrides, including the more energetic azides, the chlorides, the sulfides, and the carbides, are the next most energetic, in that order. The phosphides are the least energetic. Among the metals this order is followed by the reactions of beryllium,

magnesium, aluminum, tantalum, and thorium, with minor irregularities associated with each metal. Except for the highly energetic barium silicide system, barium follows a similar order.

The silicide and chloride systems are unusual in that the heats of formation, in Group II at least, increase greatly with increasing atomic number. In the other systems the heats of formation tend to remain relatively constant or to decrease with increasing atomic number,

Although the data are limited, it appears that compounds of the elements of the second period, i.e., the carbides nitrides, oxides, and fluorides, are more energetic than those of the third period, i.e., the phosphides and sulfides. Again, the silicides are an exception, being more energetic than the carbides.

### V. RELATION OF THE DATA TO REALITY

In using or interpreting the calculated data, the stoichiometry, free energy, and kinetics associated with experimental conditions must be considered.

In almost all cases, the calculated values represent the stoichiometric reaction that has the highest calculated enthalpy. However, many of the reactant combinations can undergo, theoretically at least, several different stoichiometric reactions which produce different combinations of products. The reactions of a metal with a chlorate, for instance, may produce different combinations of oxides and chlorides; i.e., the coefficients c, d, e, and f in the following equation can have values of zero or higher in any combination that will yield a balanced equation.

$$a A + b BClO_3 = c AO + d BO + e BCl + F ACl$$

There is no way of predicting the stoichiometry of a reaction in an experimental situation. Thus, experimentally, a reaction may not yield the maximum energy outputs that were calculated. Also, the reaction mixtures that function most satisfactorily in practical applications usually deviate appreciably from the stoichiometric ratio.

Only enthalpies were considered in the present program. The enthalpy  $(\Delta H)$  is of most interest for present purposes because it is a measure of the amount of heat energy liberated by a reaction at a particular temperature. Conceptually, a reaction such as

3 Be + 2 CoF<sub>3</sub> 
$$=$$
 2 Co + BeF<sub>2</sub> + 380.2 kcal

can be considered to occur at an infinitesimal rate at 298°K and to liberate 380.2 kcal of thermal energy. This energy will be dissipated by conduction, convection, and radiation. Since radiative transfer is an inefficient process at such a low temperature, most of the energy will be lost by conduction and convection. Conversely, the reaction may be carried out under adiabatic conditions, in which case the energy liberated will be used to heat the products of the reaction to a temperature determined by the heat content of the products and by the manner in which the enthalpy, entropy, and free energy of the reaction vary with temperature.

In reality, however, these types of reactions proceed rapidly under partially adiabatic conditions after they are initiated, and the products of the reaction are heated to very high temperatures by the energy liberated. As the products cool from a high temperature to 298°K, they effectively convert a sizeable portion of the thermal energy to radiative energy. And since radiation is our primary concern, the

the enthalpy is the most significant thermodynamic quantity. Fortunately, it also is the function which is most frequently available in the literature.

The free energy ( $\Delta$ F) defines the equilibrium state of a reaction and thus indicates the extent to which a reaction can occur. The free energy can be considered the enthalpy minus a correction term consisting of TAS, where T is the temperature and  $\Delta S$  is the entropy change. In most instances and especially in the present case, where large negative enthalpies are involved, the correction term is small compared with the enthalpy, and  $\Delta H_{298} \sim \Delta F_{298}$ , The change of the enthalpy with temperature is small because it depends on the change in heat capacity between the products and the reactants, and this change is usually small if no phase changes occur. The amount of energy liberated per mole of reaction will therefore be relatively independent of temperature. On the other hand, the free energy is strongly dependent on temperature. In fact, there is usually a temperature at which the free energy of a reaction passes through zero, indicating that the direction of the reaction has reversed. This means that although the energy output for a mole of reaction may be the same at different temperatures, the reaction will only occur to a small extent when the free energy is near zero.

Thus, although a theoretical reaction may be very energetic, it may, in fact, proceed to such a small extent that the thermal output will be greatly reduced. In a future program it may be interesting to examine the behavior of the free-energy function of some of the more interesting reactions for which free-energy data of the constituents are available.

A factor not considered but very important for practical applications is the kinetics of the reactions. There is no way of predicting the kinetics of these types of reactions. Although a reaction may be highly energetic, its kinetics may be such that the output of thermal energy is too slow to be utilized practically. In addition, these reactions must be heated to a temperature at which they can propagate at a finite rate. This temperature cannot be predicted, but is very important for practical applications and even for theoretical studies.

Because of all these unknown factors in the experimental and practical realizations of these reactions, an extensive experimental program involving several areas of study is necessary. Calorimetric studies can be used to determine the validity of the present calculations. The thermal output can be studied as a function of the stoichiometry of the reaction and the physical variations of the reactants. To further substantiate the calculations, the products of the reactions can be chemically analyzed. For theoretical and practical applications the kinetics and mechanisms of the reactions can

be studied by burning rate, radiation, and spectroscopic studies, and differential thermal analysis and thermogravimetric analysis at different stoichiometries, different ambient conditions, and different variations of the physical properties of the reactants.

In summary, the thermal data presented in this report provide a rational method for choosing reactions to be studied experimentally for theoretical and practical applications. The ancillary data included on the physical properties of the reactants and the products of each reaction aid in the selection, since these properties may be important for the theoretical and practical applications.

### VI. SUMMARY

The heats of reactions of metals with oxides, nitrites, chlorates, perchlorates, chromates, chlorides, fluorides, sulfides, nitrides, azides, carbides, phosphides, and silicides were tabulated on a Univac 1105 computer. The reactions involving chlorates, oxides, nitrates, nitrites, and fluorides tend to be the most energetic. The metals associated with the highest energies released are beryllium, magnesium, aluminum, lithium, calcium, titanium, zirconium, hafnium, lanthanum, cesium, neodymium, praseodymium, thorium, and uranium. The highest energy, -9459 cal/cc, is realized by the reaction of beryllium with magnesium perchlorate.

In all, about 20,000 reactions were tabulated. Each reaction was recorded in the primary tabulation in the form of a balanced equation. This was followed by a tabulation of input data, consisting of heats of formation, molecular weight, melting and boiling points, and also output data, consisting of reaction density and heat of reaction on molar, gravimetric, and volumetric bases.

In consequence of this large amount of detail, a page of data consists of only three equations and the data are voluminous. Therefore, only the most significant results are presented in this report and the remainder summarized. The full utility of the compilation is best realized by the establishment of secondary computer programs, designed to present the data in forms to meet specific requirements. Thus, computer programs were prepared to summarize the data in each class of reactions in descending orders of volumetric and gravimetric heats of reaction. Other programs were used to present graphically the heats of the reactions of a metal with all the oxidants of a particular class or an oxidant with all the metals, on molar, volumetric, and gravimetric bases. Still other programmed tabulations show in grid form the data for all metals with oxidizers (oxides, fluorides, chlorates, etc.), arranged in order of the energy of reaction.

The tabulations of the data presented in this report were prepared to meet the requirements of a specific problem. However, the special merit of the system lies in its versatility, since the possible treatments of the data can be varied to cope with innumerable applications involving other uses of these data.

# VII. FUTURE WORK

The studies presented here have been essentially completed as far as the enthalpies are concerned. Almost all systems of potential interest for which data are available are included. It would be of interest, however, to calculate the free energy and equilibria of certain reactions as a function of temperature. These calculations would predict the maximum temperature and the extent of the reactions. They would be limited to reactions for which free energy and specific heat data are available.